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EVOLUTION AND PALAEOGEOGRAPHY OF THE VARISCAN OF NEO-EUROPE

H. W. FLÜGEL

The tectonic framework of the middle part of Neo-Europe is dominated by two lineaments: The Periadriatic Lineament northward of the Southern Alps and the Balcan—Dinaric Lineament between the Vardar-Zone and the Serbo-Macedonian Massif *(Fig. 1.)*. They are firstly clearly apparent in the Late Palaeozoic when *they separate a terrestrially developed outer region from a marine inner region.*

This facies division can be followed further into *Asia Minor* and *Transcaucasia* [BRINKMANN, R., 1968]. Here, playing a dividing role similar to the Serbo-Macedonian Massif, the *North-Anatolian Swell* separates a southern zone of the marine Late Palaeozoic from the northern terrestrial zone.

The inner region of Neo-Europe includes the Southern Alps and the Dinarides as well as the Igal—Bükk Palaeozoic Trough [WEIN, Gy., 1968]. The latter separates

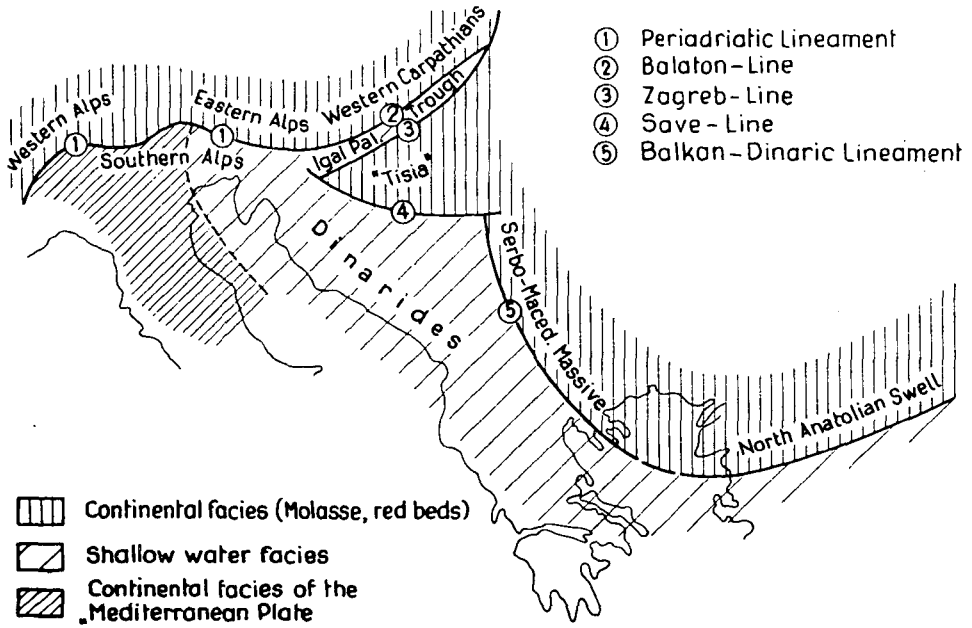

Fig. 1. Palaeogeographic sketch of Neo-Europe during the Later Palaeozoic (Upper Carboniferous/Permian).

the Pannonian Massif [Tisia: SZALAI, T., 1970] from the Palaeozoic of the Western Carpathians and its subterraneous connection with the Palaeozoic of the Styrian Basin.

In the *Southern Alps*, the development begins with a thick pelitic—psammitic sequence of probable Cambro—Ordovician age. Radiometric data (430 m. y.) indicate metamorphism and (?) orogenesis during the Caradocian [GRAESER, S., J. HUNZIKER, 1968; MCDOWELL, F., 1968; PIDGEON, R., V. KÖPPEL, M. GRÜNENFELDER, 1968]. In the fossiliferous series, these disturbances are evidenced only trough secondary events (volcanism, stratigraphic break [SELLI, R., 1963]. The subsequent carbonate-platform and deep-water development of the section during the Silurian, Devonian and Lower Carboniferous ended before the Asturian folding with a Middle Carboniferous flysch-sedimentation [FRANCAVILLA, F., 1966]. At the same time, connected with an uprise, building of some molasse troughs was taking place in the Lugano area. The time between the Asturian orogeny and the development of the Mesozoic Tethys was characterized by repeated, but non-contemporaneous transgressions, thick accumulations of ignimbrites connected with postorogenic granites [BORSI, S. *et al.*, 1966, 1972; JÄGER, E., H. FAUL, 1959: "*late-Hercinyan magmatic province of Trento and Lugano*"] dated as 270 m. y. old, and followed by a largescale erosion [RAU, A., E. TONGIORI, 1972].

Towards the SE, this zone grades into the *Dinarides* with facies changes, but without a clear boundary. After the Variscan folding, the dominantly shaly—calcareous Early Palaeozoic was transgressed from the south by units of the Upper Carboniferous and Permian [RAMOVŠ, A., 1964; KOCHANSKY DEVIDÉ, V., 1964]. With this transgression came during the Lower Permian the development of the shelf-edging Trogkofel-reef [KAHLER, F., 1974; KOCHANSKY-DEVIDÉ, V., 1969], wich separates the thick shallow-water deposits of the clastic Košna-sequence [KOCHANSKY-DEVIDÉ, V., 1973; RAMOVŠ, A., V. KOCHANSKY-DEVIDÉ, 1965] from the "oceanic" (?) area to the east [DIMITRIJEVIĆ , D., 1972; ILĆI , M., 1969]. This model requires that a mainland was present in the Apennine area: a supposition supported by the terrestrial Permian of the Autochthon of Toscania [MAZZANTI, R., 1961]. Still unsolved is in this model the origin and age of the thick Gröden-beds of the Savefalten [GRAD, K. *et al.*, 1962].

A picture very similar to that is found in the Eastern Dinarides where the Late Palaeozoic beds of *West Serbia* build up a transgressive sequence above the older, folded Palaeozoic strata [FILIPOVIĆ, I., 1973]. These transgressive units, together with the marine sequence of the Late Palaeozoic of the *Igal—Bükk Trough*, wich is known by the boreholes Karád and Bugyi, further in the Bükk Mountains [BALOGH, K., 1964], form a Late Palaeozoic shelf sequence along the mainland of *the Pannonian* and *the Serbo-Macedonian Massives*, both of them being characterized by a thick terrigene Upper Carboniferous molasse and Permian Red beds with volcanic rocks [PANTIĆ, N., 1964; TENCHOV, Y., 1973].

The significant facies contrast existing between the Late Palaeozoic of the Igal—Bükk Trough resp. the terrestrial development north of the Lake Balaton (in the Bakony Mts. and in the West-Cartaphians) indicates that *the Periadriatic Lineament has its continuation probably in the Balaton-Line (Fig. 1)*.

The counterpart of the marine inner region of Neo-Europe with its mainland areas in the west and east is found *northward of the Periadriatic Lineament* in the form of the Late Palaeozoic terrestrial sequences in the Eastern Alps and the Western Carpathians.

The Early Palaeozoic and the Lower Carboniferous of the *Eastern Alps* are

more or less comparable to the development in the Southern Alps [FLÜGEL, H. W., H. P. SCHÖNLAUB, 1972]. This similarity also holds true in respect of the Upper Ordovician metamorphism under intermediate pressure and medium-to-high temperature and the acid magmatism which can be found in several crystalline areas in the western part of the Eastern Alps [BORSI, S. *et al.*, 1973], and the Variscan folding, metamorphism and orogeny [JÄGER, R., 1971].

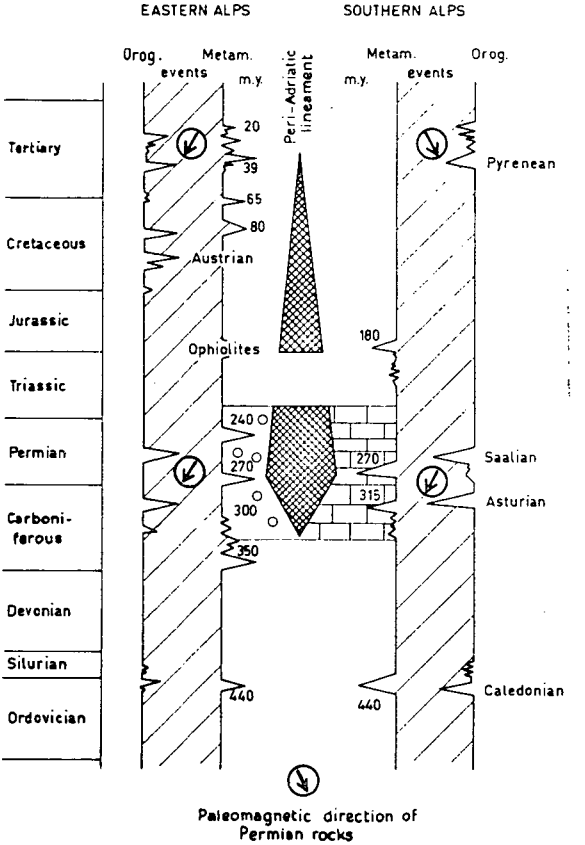

Fig. 2. Diagram of the development of the Eastern and Southern Alps.

In the contrast, there are clear differences between the Carboniferous and Permian where the development is comparable to that of the Autochthon of the Apennines, or to that of the Pannonian resp. Serbo-Macedonian Massif. In this respect it is noteworthy that — both in the Southern and in the Eastern Alps — a pre-Upper Carboniferous erosion surface cuts the earlier beds, and the latters come even older from east to west whereby the values of the cooling age measured on Variscan biotites and muscovites suggest a postorogenic pre-Permian uplift and an erosion of 5 km/10 m. y. [BORSI, S. *et al.*, 1973].

A special case within this terrestrial development is shown by the marine sequence of Namurian—Westphalian age of the Northern Gemerides (West-Carpathians) *wich probably had no connection to the Igal—Bükk Trough*, but — as its fauna shows — was connected to the north and northeast [ABONYI, A., 1971].

The facies division of the Late Palaeozoic of Neo-Europe presented here shows that three geotectonically differing, major areas were developed, probably associated with the Variscan orogeny:

1. the marine—terrestrial facies of the "Mediterranean Plate" with the Southern Alps, Dinarides, Apennines and Igal—Bükk Trough;

2. the eastern continental facies of the Pannonian, resp. Serbo-Macedonian Massif and the North-Anatolian Swell;

3. the development north of the Periadriatic Lineament and the Balaton-Line, wich is similar in many respects to the facies No. 2.

In the discussion of the palaeogeography of the Late Palaeozoic of Neo-Europe, one cannot forget the palaeomagnetic data wich indicates a probable counterclockwise rotation of the Mediterranean Plate of 50° during the Paleogene [SOFFEL, H., 1973]. It sould be remembered, however, that borders of this plate are still unknown. It is obvious to bring the facies differences during the Permian into conection with this plate rotation. On the other hand it is to be mentioned, that the regression of the Triassic sea put an end to the clear separation during the Permian, and the Periadriatic Lineament is no longer during the Triassic time clearly apparent [BOSELLINI, A., K. HSÜ, 1973]. Only from Jurassic onwards, differences in the facies can be seen again on both sides of the mentioned lineament, coinciding with the clear differences of the orogenic and metamorphic events on both sides of the Periadriatic Lineament *(Fig. 2)*.

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GEOLOGICAL CONDITIONS OF THE UPPER PANNONIAN OIL-SHALE DEPOSIT RECOVERED IN THE BALATON HIGHLAND AND AT KEMENESHÁT

Á. JÁMBOR and G. SOLTI

ABSTRACT

In the course of systematic geological investigations carried out in the Transdanubian Central Mountains, in the shallow borehole west from Pula (Balaton Highland area), immediately under the surface, an about 20 m thick, organic-rich laminated formation occurred which, according to examinations, proved to be a characteristic oil-shale deposit. During geological studies we came to the conclusion that this oil-shale was deposited in the basalt crater lakes developed in Pliocene time, when special conditions enabled the formation of this characteristic sedimentary facies. After having disclosed these circumstances of development, in the environs of the villages Kemeneshát and Gérce, in the basalt area of the Little Hungarian Plain's central part, in an earlier basalt crater, about 70 m thick oil-shale deposit was recovered.

May be that, a systematic examination of Hungary's sediment series will result the recovering of further oil-shale deposits.

1. PRELIMINARIES

In Hungary, oil-shale prospecting has no traditions. It was I. VITÁLIS [1946] who mentioned for the first time a 50-cm-thick "bituminous brown coal" intercalation in Miocene volcanites in the southwestern part of the Mátra Mountains and published the respective results of chemical analyses:

Moisture	2.74%	Moisture	3.79%
Ash content	38.16%	Semi-coke	56.70%
Heat of combustion	4816 kg/cal	Tar	26.7 %
Calorific power	4551 kg/cal	Water as a decomposition	
Sulphur content	7.51%	product	2.11%
Hydrogen content	4.6%	Gas and losses	11.4 %
Carbon content	34.71%		
O+N	12.24%		

Regarding the precise composition of the rock characterized by I. VITÁLIS, only the work of E. SZÁDECZKY-KARDOSS and P. TAKÁCS can be taken for a basis, who came to the conclusion that this was no brown coal but a "boghead rock", including alginite, eualginite, bituminite, fusite and their minerals. The fossil algae were mainly of *Botryococcus* origin.

To the end of 1973, in the frame of the geological reambulation of the Transdanubian Central Mountains, a survey-borehole was sunk to reveal the existing stratigraphic conditions on the southern margin of Mt. Kab, in the northern foreland of the Upper Triassic dolomite fault block, northwest of Pula. In borehole Put-1, overlying the Pliocene basalt, a 38.0 m thick, when dry greenish grey, very fine-

grained, organic-rich and rather tuffitic formation, loose, light laminated and in wet state dark green, was traversed. Derivatographic analyses (M. FÖLDVÁRI) gave a striking result: the rock was burnt, smelling disgustingly of stearine and leaving behind very little ash. On our request, DR. F. GÓCZÁN, analyzing the rock, found that the residual material obtained after palynological treatment, consisted mostly of *Botryococcus braunii* KÜTZ., planktonic brown algae of microscopic size.

On the basis of these informations, the Research Department of the Central Geological Office of Hungary ensured significant funds for further investigations of the above formation. After carrying out this activity, we turned to the Mining Research Institute. We feel greatly indebted to DR. P. TAKÁCS, Head of Department at the Mining Research Institute, for the informations he gave us, which has had an incentive influence on further research. He called our attention to the fact, that these oil-shale deposits, if available in substantial amount, would enable the development of a significant oil industry, *i. e.* organic chemistry.

In their expert opinion, P. TAKÁCS, MRS. J. ARATÓ and MRS. L. BELLA maintained firmly that, from technological view-point, the oil-shale found in the vicinity of Pula is a characteristic one and as such, it can be used as starting material on distillation for oil.

Beside technological analyses, geological mapping results of the Pula region were estimated, too, and after their comparison with the simultaneously obtained laboratory data, the following geological, paleogeographical and geohistorical and genetical conclusions could be deduced.

2. GEOLOGICAL CONDITIONS OF THE OIL-SHALE DEPOSITS AT PULA

About 500 m west of Pula, the oil-shale sequence covers the second basalt lava flow with local unconformity *(Fig. 1)*. Drilling in 1973 proved the presence of sedimentary rocks (sand, siltstone, calcareous silt) between the second and third basaltic beds.

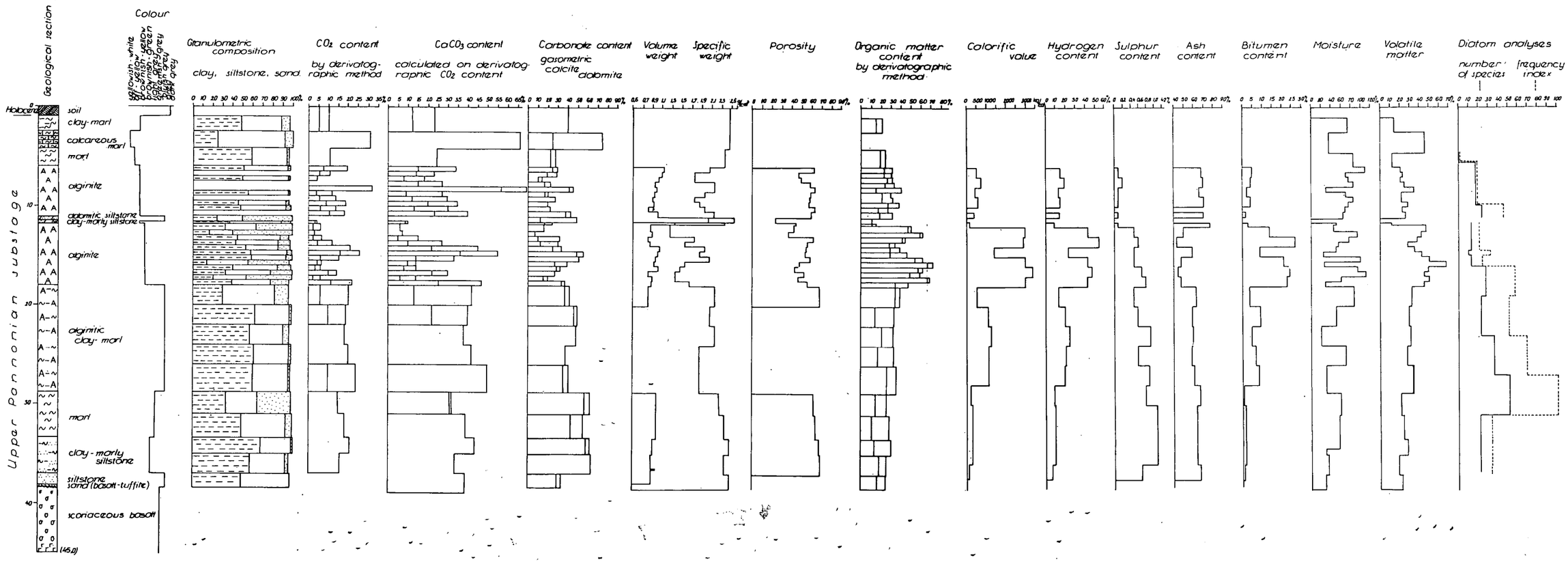
As a consequence of gas emanations, the texture of the uppermost 8 metres of the basalt, underlying the oil-shale, became scoriaceous. This member is followed by a 34.2-m-thick (4.2 m to 38.4 m) Upper Pannonian formation, called "oil-shale member of Pula" which can be subdivided into four parts. It should be remarked that in Hungary this was the first case when above the basalt no Pleistocene sequence occurred.

The lowermost group of strata starting with the 5 cm of basaltic sands, contains siltstones, clay-marls with siltstone and one marl bed. The second group consists of alginitic clay marls, the third one of clay marls with alginite, and with dolomitic intercalations, while the fourth, *i. e.* youngest one, is made up of marly, and clay-marl strata. The whole member is characterized by greyish-green, green-grey,that is, by reductive colours, and a more or less thinly laminated structure.

In borehole Put-3 *(Fig. 1)* directly above the basalt, 5.0 cm of arched and cross-laminated sand was deposited, containing light-grey basalt grains of 0.1—2.0 mm diameter, from which the oldest pelitic rock of the "oil-shale member of Pula" has developed with alternating changes in lithology, forming a 1.3-m-thick layer which on the whole may be denoted as siltstone (Photo 1, Plate I). In the lowermost 10 cm of the siltstone 5 arched cross-laminae of basaltic sands of 30° inclination and each 1 cm thick, are intercalated. The siltstone layer consists of differently colour-

Fig. 1.

Geological and material testing section of borehole Put-3, Pula



red (grey, light-grey, off-white, greenish grey) and distinctly horizontal and parallel laminae with an average thickness of 1 to 30 mm (mostly 5 mm and maximum 300 mm and made up of various materials. The material of each lamina was not separately analyzed, nevertheless even after examination in the field it was evident that the lighter parts were richer in unconsolidated calcareous silt.

Above the siltstone (between 28.8 m and 37.0 m) follows a light greenish-grey, laminated siltstone member with clay marl which we divided into two parts at 33.4 m, the upper part being richer in lime. This rock consists of 1 to 150 mm, more frequently 2 mm thick laminae (Photos 2 and 3 Plate I). Lithologically, three different kinds of laminae can be distinguished. The siltstone laminae are 5 to 30 mm thick, consisting of readily identifiable, very fine grains of basalt tuff. The yellowish laminae are calcareous, while the greenish ones contain much clay but both are thinner than the siltstone layers. In the more calcareous laminae of parallel stratification, there are more or less compressed, hollow fragments of *Chara* stem sometimes in rock-forming quantity. These fossil debris are only of some tenth of millimetres size, their length attains 5—10 mm, and they are unoriented along the bedding plane. Limpid mono- and bivalves of Ostracoda situated parallel to stratification are not rare either. The inner part of bivalves is empty. At 36.1 m some carbonized leaves occur.

The layers, except for the 32.1 to 32.4 m interval, are completely horizontal. The afore mentioned interval still seems to have been produced by subsiding mud still in plastic state, which may be proved not only by the seemingly chaotic plication but also by its intraformationally brecciated texture (Photo 4, Plate II) as well.

This layer is followed by a properly alginitic subdivision (from 6.0 to 28.8 metres), quite different due to its slate green colour, differently laminated jointing and striking lightness, and in the fresh state (that is, 3—10 months after being exposed) to its characteristic smell reminding mainly of bensene; and, normally, they are conspicuous for being able to be ignited and for the flexibility of their laminae.

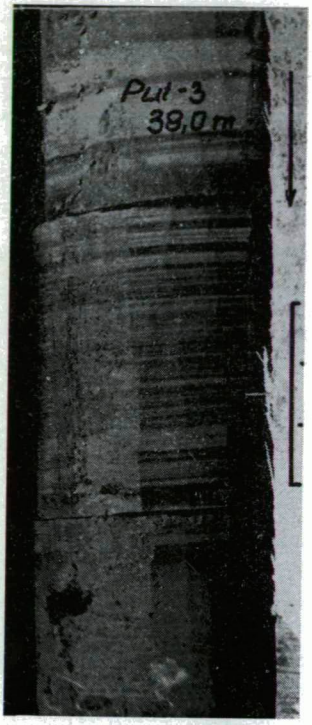
The sediments between 6.0 and 28.8 m are similarly laminated but differ from the underlying rocks, including only two predominant types of laminae. The laminae are easily separable and thinner, with a thickness only of 0.1 to 4.0 mm (Photo 6 Plate II). One type is roughly green in colour and, viewed under hand magnifying glass, it seems to be made up mainly of green and pale yellow, isolated or grouped globules. The other one with its pale green or greyish yellow colour is more calcareous. The laminae between 18.0 and 28.8 m include a significant amount of pelitic component.

In the alginitic sediments the siltstone with clayey marl (11.6 to 11.8 m) is overlain by siltstone (11.1 to 11.6 m) the cement of which is light grey dolomite. This latter is made up locally by fine sand, the grains of which predominantly result from erosion of basaltic tuff, however, some muscovite laminae of metamorphic origin can be observed, too.

The layers between 18.0 and 28.8 m within the alginitic subdivision, are horizontal, whereas from 6.0 to 18.0 m they show an inclination of 5—8°, perhaps being the consequence of a rearrangement after mud-subsidence. Between 15.5 and 15.6 m plication due to mud subsidence and/or intraformational brecciation could be observed (Photo 5, Plate II).

Between 6.0 and 11.1 m, the laminae after drying out — in contrary to those of the other parts in the sequence — are curved up as a burnt paper. At the same time, following deposition, along some bedding planes several arched desiccation

PLATE I



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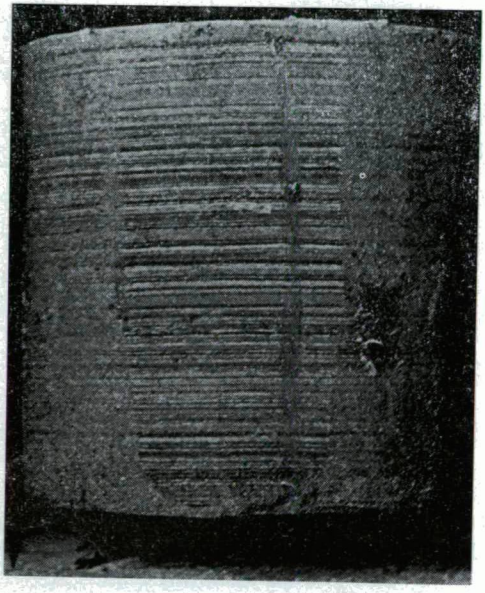

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cracks were formed. From 7.4 to 7.8 metres, again intraformational breccia can be observed, at 10.5 m with a somewhat compressed *Diptera* (?) fragment.

In the hanging wall of the alginitic layers (1.0 to 4.2 m) the lamination of the laminated marl, calcareous marl and clayey marl is not so distinct as in the alginitic part, since the quantity of the loose pelitic calcareous mud within the laminae — though significantly fluctuating — roughly surpasses that of clayey components. Thus we may find white, pale yellow, yellowish grey and grey laminae, respectively. In the lower part of the hanging wall (about 2 m in extension) many carbonized small plant-stems and herbaceous-like leave debris can be observed on the surface of some laminae. In the upper part of these sediments the slope is 1—2°, while in the lower part 5—8°. At last it is covered by a dark grey, 1 m thick, humus-soil.

Geological data have made it obvious that the alginitic shales, i. e. oil-shales, developed under rather special paleogeographical conditions, at the same time when the upper part of the *Congeria balatonica* sediments were deposited. Their present-day local stratigraphic situation is shown in *Fig. 4* As an evidence of borehole Put-1 the basalt of the foot-wall may be regarded as the filling of a crater channel. Taking into consideration the sequence found in borehole Kpt-1 (at Kapolcs) this basalt may be identified with the second basalt layer of the above sequence, while the immediately underlying basaltic sand may be regarded as a deposited layer of the 2nd basalt-tuff. The sediments accumulated simultaneously with alginitic rocks are known from boreholes Put-2 and Vgt-1 (Vigántpetend) in the region of the Tálod forest. Here the lower layers of freshwater limestone at Nagyvázsony can be correlated with the rocks overlying the oil-shale (1.0—4.2 m) in borehole Put-3. At the basis of limestone at Nagyvázsony, several dm thick bentonitized sediments (corresponding to the 2 nd basalt-tuff) are followed by a bluish-grey clayey marl, underlain in borehole Put-2 by alternating sequence of clayey marl, clayey siltstone and carbonaceous clay including brackish and freshwater fauna correlating well with the Upper Pannonian *Congeria balatonica* beds. These in turn, developed by continuous sedimentation from the *Congeria ungulacaprae* beds. Although the lower strata of freshwater limestones at Nagyvázsony are of the same age as the alginitic series of Pula, their development is different, because the latter was sedimented under special circumstances in a basalt crater lake.

In the region of the Tálod-forest also the hanging wall of the freshwater limestone of Vázsony is known. It is overlain by bentonitized sediments of the 3rd basalt-tuff, which, in turn, is covered by 1—8 m thick 3rd basalt. Then it is followed by Würmian loess.

EXPLANATION OF PLATES

Sedimentologic phenomena of the oil-shale deposits in borehole Put-3 at Pula

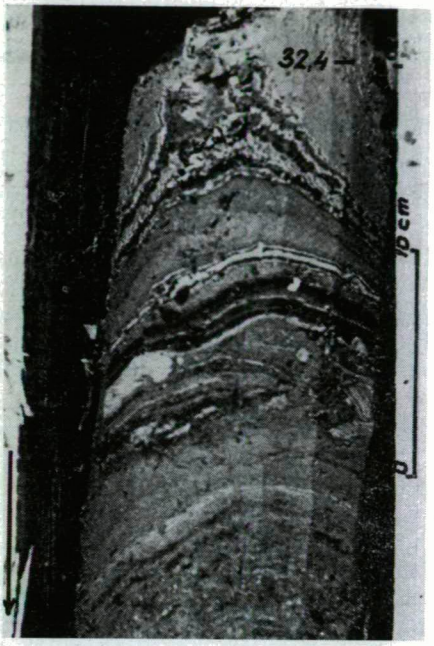
Diameter of the drill cores is always 10 cm. The arrows show the direction of the foot-wall.

Plate I

Photo 1 Laminated siltstone at the beginning of the sequence
Photo 2 2nd layer: clay marly siltstone including plant debris
Photo 3 2nd layer: lamination of the clay marly siltstone (36.0 m)

Plate II

Photo 4 Mud subsidence in laminated marl
Photo 5 Mud subsidence in laminated alginite
Photo 6 Laminated alginite (9.2 m)



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5

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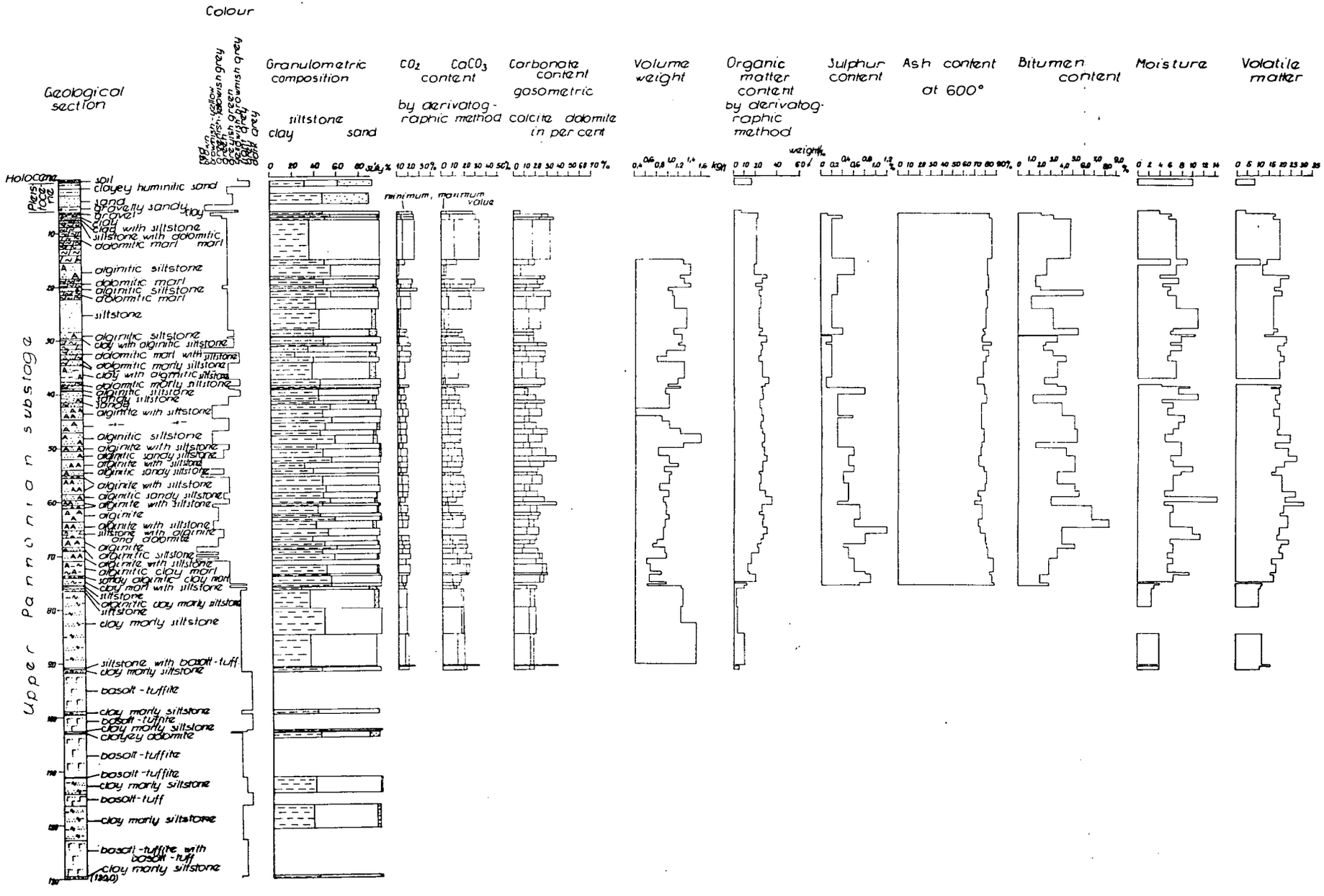
Fig. 2.

Geological and material testing section of borehole Gét-1, Gérce



The precise size of the lagoon surrounded by the ring-shaped tuff wall of the volcanic crater and impeding sediment transportation from the near-by brackish-water lake was examined by the Transdanubian Ore Prospecting Department of the Eötvös Geophysical Institute (Cs. TÓTH) with the aid of surfacial resistivity measurements. According to these investigations, the ring is elongated southwest of the Eger river's valley including also the sinter mound on the small hilltop soaring in the north above the valley bend and possibly having been active simultaneously with the deposition of the upper part of freshwater limestone sequence of Nagyvázsony.

The investigations of the special sedimentation conditions of the lagoon enclosed within the tuff-ring, enabled to determine the area of further studies.

3. GEOLOGICAL CONDITIONS OF THE GÉRCE OIL-SHALE

Thus, it was evident that, for the recovering of further oil-shale deposits it would be necessary to seek for similar tuff-rings as that of Pula and to drill their inner part. Earlier geological investigations had made easier this work. Thus, from the literature [L. LÓCZY, 1913, L. SZEBÉNYI, 1953, K. VARRÓK, 1953], the tuff rings of Sitke and Kemenesmagos are well-known *(Fig. 3)*.

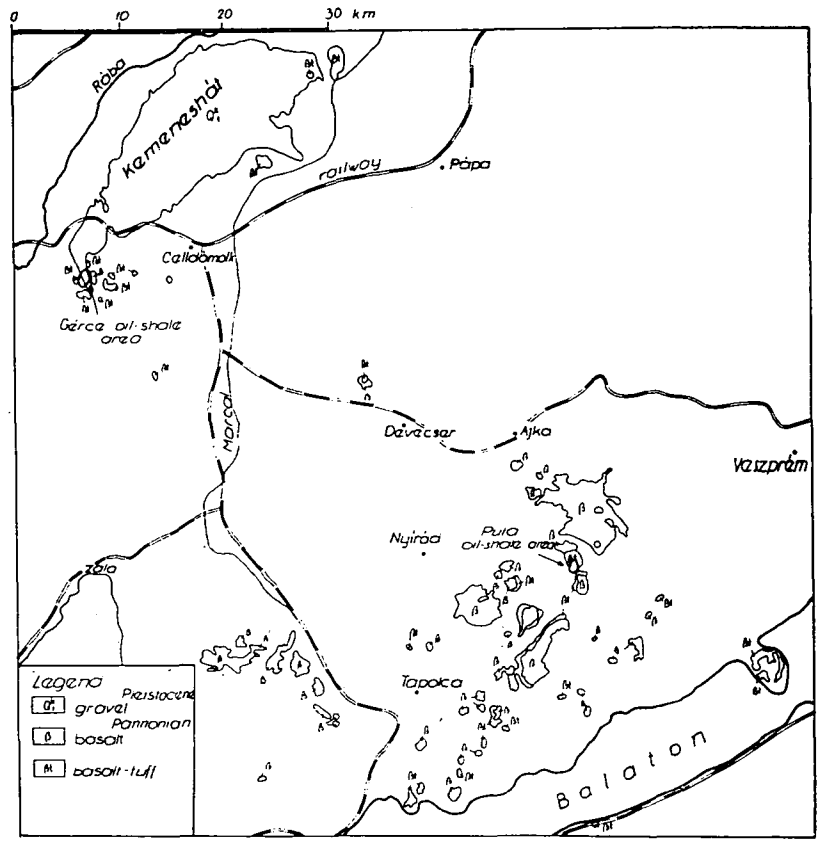
The tuff-ring northwest of Gérce (reaching a thickness of 90 m) is filled up with sediments connected with the oil-shale member of Pula. Similarly to the sediments filling up the area at Pula, the series occurring within the tuff-ring at Gérce, can be divided in three parts, however, it may be remarked, that at this last place the basalt foot-wall is unknown.

In the environs of Gérce, in the deeper basement of the oil-shale recovered by borehole. Kemt-1 at Kemenesmagos, 32 m below the oldest basalt tuff (52.7 to 55.7 m) a brackish water Mollusca fauna bearing clayey marly siltstone was found indicating the middle-top part of the Upper Pannonian and determined by M. M. KORPÁS-HÓDI *(Congeria neumayri* ANDR., *Unio sp.?, Pisidium sp., Valvata obtusaeformis* LŐR., *Valvata sp.)*. Thus, the basalt tuff of Gérce is the younger being substantially higher. The diatoms and macroflora-bearing oil-shale of Gérce, as well as the palynological character of the basalt tuff, i. e. of the ring formed by it and filled up, proves its belonging to the Upper Pannonian. According to I. PÁLFALVY, the macroflora includes the following: *Cercidiphyllum crenatum* (Ung.) BROWN, *Equisetum sp.*, fragment of *Glyptostrobus, Gramineae, Liquidambar sp., Phyllostochys sp., Quercus sp., Q. cerris* type, carbonized fruits. The oldest subdivision of the infilling was traversed by the drilling between 90.8 and 130.0 m *(Fig. 2)*. If we consider the inclination of 50—70°, it would mean a thickness of about 20 m. This part is made up of alternating basalt tuff, clayey marly siltstone, dolomite marlstone and basalt tuff. The basalt tuffites consist of grain-fragments of different size and are, in terms of the nomenclature of sedimentary rocks, sands or siltstones with sand and small gravels. Their material is basalt, rounded or completely unrounded, scoriaceous, vesicular, aphaneritic or vesicular porphyritic. Naturally, only grains above 0.3—0.5 mm could be determined by the naked eye. Sometimes the arched cross-lamination of sands could be well observed. Here, the grains are well to fairly graded, in contrary to sediments originating from dispersion or tuffs fallen into water, which show a distinctly poor grading. In basalt tuffite layers (=washed-in basalt tuff fragments) also intercalations of basalt tuffs fallen into water were observed. There occur fragments reaching even 15 cm and every grain seems to be unrounded, with

sharp contours, while the character of stratification within a layer could not be observed. Besides the basalt tuff fallen into water (114.2—116.4 m) also some other marks of a simultaneous volcanic activity could be recorded. In some water-fallen tuffs of silt size, disproportionately large, isolated and unrounded basalt fragments occurred, which had fallen as lapillies into an unconsolidated mud. Similar fragments occur in some pelitic sedimentary rocks of non-volcanic origin.

Fig. 3.

Transdanubian oil-shale deposits related to Pannonian basalts



Basalt tuffite layers — except for a single basalt tuff and a single dolomitic marlstone intercalation — alternate with clayey marly siltstones. On the basis of their lithology and texture they can be regarded as common Pannonian sediments. They show a conchoidal-laminated jointing and, fine muscovitic laminae frequently occur parallel to the joints. With unaided eyes no fossils can be observed.

In connection with dolomite marlstones of borehole Tihany T-62 [Á. JÁMBOR, 1973] mention should be made of the two dolomite layers interbedded with the water-fallen basalt tuff (102.8 to 103.0 m). Even these intercalations are of pale greenish grey colour, conchoidal-splintery, cryptocrystalline, hard, dense, unbedded rocks. The presence of dolomites may be connected with the excess of magnesium originating from the weathered material of basalt tuff glass.

This is conformably overlain by a "stratovolcanic basalt member", which may be correlated with the "oil-shale member of Pula". The boundary is only theoretical, because it was drawn there, where basalt tuff fragments upward in the sequence were last observed even with an unaided eye.

The oil-shale member starts with a 14 m thick clayey marly siltstone (76.5 to 90.8 m) consisting of 1—20 mm thick, parallel lamination and slightly different average grain size. Among the fine grains both basalt tuff grains and grains originating from metamorphic sources can be recognized. This layer is situated practically horizontal. The oil-shale sequence in the strict sense (76.5—7.0 m) may be divided into three parts, though emphasizing the fact that on account of their organic content being far more abundant than the average and their predominantly laminated texture and the low volume weight, they represent the same unit with close genetic relations. These series are similarly united by the frequency of fossils belonging to the sedge family, *Herbaceae* and, subdued, leaves of deciduous trees. The leaves of trees — except for some limonitized ones from the uppermost part (15.4—40.6 m) — are carbonized. Their substance is of black, lustrous, and flexible coal. Another common character of these sediments is the strong, chemical smell, different from that of lignites, which is well perceivable even half a year or a year after the core material was brought to the surface.

The first subdivision (76.5—68.3 m) is — in contrary to the younger part of the sequence, — characterized by frequent occurrence of pale yellowish-white, loose calcipelite laminae. The subdivision is made up of greenish-grey alginitic siltstones, but between 69.0 and 71.0 m the colour of every third lamina is pale red. The other layers consist of 0.1—1.0 mm thick, slightly undulating laminae, of greyish-green colour. These are represented by three types. The pale leaf-green and possibly the above-mentioned pale red ones are highly alginitic, while the grey sediments include plenty of clay and other mineral fragments, and the pale yellow ones are made up of calcipelite. Between 73.6 and 74.0 m, besides the small-grained sand laminae occur maximum 5 mm thick fine-grained sand laminae including basalt tuff and quartz material, while the earlier burrows of mud-eaters filled with sands (of 3—7 mm diametre) irregularly change their direction. Although the layers of this subdivision are practically horizontal, in their middle part of about 80 cm (69.0 to 71.0 m) the laminae show an inclination of 15—20°. This may be the consequence of slumping.

In the two lowermost layers of this subdivision (76.0—76.5 and 75.4—75.6, respectively) parallel to stratification, several, rather large, *Ostracoda* mono-valves were found.

The second subdivision (68.3—42.2 m) is the most alginitic part of the oil-shale with alginite-rich laminae. Thus it is also alginitic siltstone, alginite with siltstone and alginite with sand and siltstone, consisting of fine (0.1—0.5 mm thick and locally even 15 mm thick) laminae. Unlike the lowermost part, here calcipelite laminae are not present, however, the siltstone and fine-sandy laminae include more or less dolomitic marl components. As mentioned above, the alginite-rich laminae are of different green and pale brick-red colour, while the siltstone and sand laminae

are grey. Brick-red laminae occur only in 4 layers (60.5—61.1, 55.0—55.5, 52.0—54.0, and 42.2—44.6 m). In the lower part of this subdivision (60.5—60.6 m) again a yellowish grey calcareous layer was found.

The laminae are generally horizontal, only in the uppermost layer (42.2—44.6 m) plication due to slumping can be seen. Between 61.1 and 63.8 m, small "unconformities" due to scour by subaquatic current may be observed.

The grains of the sandy laminae, made up of basalt and quartz, are similar to those of the lower parts. In contrary, the siltstone laminae including some tenth of millimetre thick muscovite laminae parallel to stratification are characteristic.

The uppermost part of the alginitic (=oil-shale) sequence considered in the strict sense, and traversed by drilling Gét-1 (42.2 to 6.4 m) contained dolomitic marly siltstone, siltstone with sand and dolomitic marl, and alginitic siltstone with more or less dolomitic marl.

The ratio of dolomitic marl increases upwards while the amount of alginitic rocks is diminishing. The uppermost (0.6 m thick) layer of the subdivision is mottled clay, which seems to be of bentonitic origin. It may be assumed, that it originated from a different transformation of basalt-tuff ejected from an eruption centre other than Gérce.

The dolomitic marl and dolomite-marly siltstone intercalations are not stratified, their colour is pale yellowish or pale brownish-grey. The texture of siltstone is, however, laminated. Alginite-rich laminae are green, greyish-green or pale brownish-red, while those of siltstone are grey of different shades. The laminae are horizontal or, as a result of slumping, chaotically plicated (34.5—37.5, 31.5—32.5, 20.0—20.7 m). It should be remarked, that though two layers in the 7.0—8.0 m interval are plicated, judging by their features, these seem to be rather the result of crioturbation movements.

In three dolomitic siltstone layers (37.5 to 39.2 and 32.5 to 3.4) dark green rounded bentonitic nodules (with a diameter of 1.0 to 5.0 mm) were observed, while in the siltstone bearing dolomitic marl (29.8 to 31.5 m) pieces of basalt tuff (with a diameter of 1.0 mm) occurred. Regarding its texture, the dolomitic siltstone (38.7 to 39.2 m) is an intraformational breccia but chaotically plicated. The sandy components are of two types: basalt tuff and quartz. In the siltstone layers regular, some tenths-of-mm-large muscovite laminae parallel to stratification occur frequently.

In the lowermost layer (at 39.4 m) the total surface of the drill core was covered by a yellowish dark-grey pyrit segregation. (This visual observation was confirmed by *X*-ray diffraction measurements by I. VICZIÁN.)

The alginitic (=oil-shale) sequence is unconformably overlain by an Early Pleistocene gravel-terrace of the Rába river covering almost uniformly the whole Kemeneshát area. It includes gravels, gravelly sandy clay, and sandy clay. The sand grains manifest rather well the aeolian influence. The 4.7-m-thick Pleistocene terrace is overlain by 1.1 m of black clayey sand (swamp facies) which in turn, is covered by pale grey sandy soil (0.6 m). These deposits have been assigned to the Holocene, as in the vicinity of the borehole, in the area enclosed by the tuff-ring minor pools becoming periodically swampy still occur even today.

If we compare the features of the Pula and Gérce deposits studied by field methods, the following results will be reached.

TABLE I

Comparison of geological features of the alginitic basalt member hanging wall

Features	Pula	Gérce
Conformable laying stratigraphic cover	known theoretically	unknown
Mineralogical features of the surrounding layers	calcitic	dolomitic
The features of organic material	green, coarse alginite, the lower part rich in diatoms	green, and pale red fine-grained alginite, the lower part rich in diatoms
Plant debris	carbonized leaves, Chara stems	carbonized leaves
Laminae	green, grey, off-white	green, red, grey, off-yellow
Green alginite-rich laminae	occur	occur
Red alginite-rich laminae	are not present	occur
Laminae with much clay	characteristic	not characteristic
Laminae with much siltstone	not characteristic	characteristic
Low volume weight	characteristic	characteristic
Laminae with basalt-sand	are not present	characteristic
Calcipelite laminae	characteristic for the lower part	characteristic for the lower part
Average thickness of laminae	higher (0.1—50 mm)	lower (0.1—5 mm)
Plication due to subsidence	characteristic	characteristic
Intraformational breccia	occur	occur
Presence of muscovite	unobservable by naked eye	characteristic of the siltstone
Bentonite nodules (1—5 mm)	rare	in several layers frequent
Freshwater gastropodal fauna	rare	is not present
Ostracoda bearing siltstones	below the alginitic part	below the alginitic part
Siltstone layers	are present	are present
Initial siltstone layers	cross-stratified basalt-sand	cross-statified basalt-sand
Basement	basalt	unknow
Thickness of the basalt-sand layer	8 cm	some layers are of several metres thickness
Foot-wall of the basalt-sand	basalt	basalt-tuff
Thickness of the whole complex	40 m	90 m
Structure of the holder	basalt crater	basalt crater

4. RESULTS GAINED BY WELL-LOGGING MEASUREMENTS

According to prescriptions by the Central Geological Office, complex well-logging (including natural potential, resistivity, natural gamma, gamma-gamma and yield measurements) was performed in boreholes Put-3 and Gét-1, by the geophysical group of the Hungarian Geological Exploration and Drilling Company, Várpalota. Their interpretation was carried out by geophysicist Sz. URAY.

The resistivity logging of the basalt in borehole Put-3 could be carried out from 17 m down to the bottom of the hole, since the upper part of the hole was empty because of water swallowing by the basalt. In the measured intervals the three resistivity values were about 20 ohm/m, and varied slightly. It decreased only in the lowermost part, that is, in the sand layer overlying the basalt, to the value of 3—12 ohm/m.

On the basis of natural gamma measurements, the radioactive substances in the oil-shale formation of Pula do not reach the well-known low radioactivity of basalts (35 microroentgen/hour). It was, however, observed that, in the 38.4 and 16.0 m interval the value of natural gamma radiations decreased from 35 microroentgen/hour with slight fluctuations to 13 microentgen/hour. This decrease is parallel with the sulphur content, ash content and change of specific weight of the sediments, thus it may be connected with the pyrite and potassium content of the sediments. It is a well-known fact, that pyrite is inclined to fix uranium.

It is similarly difficult to explain the higher micro-roentgen/hour values (22—31) of the 16.0 to 4.0 m interval. Most valuable data were reached by gamma-gamma section. The 30,000—125,000 pulses/min value of the 4.0 to 28.0 m interval may be regarded as anomalous. A significant anomaly was observed between 6.0 and 15.0 m, where the oil-shale content also showed anomalous values (90,000—125,000 pulses/min).

The studied sections of the oil-shale sequence of Gérce, were similar. The gamma-gamma values between 8—23 m, however, were only 21,000, while from 23 to 76 m 60—65,000 pulses/min. The lower boundary, at 76 m, coincides with the setting in of anomalous organic content, but at the upper limit a deviation of 5 m was recorded. Anomalous values of organic matter begin to occur at 18 m already. At present, the cause of this deviation cannot be interpreted.

5. RESULTS OF TECHNOLOGICAL AND CHEMICAL ANALYSES

The analyses of alginitic layers are being run now according to well-developed and tested procedure. In the field, after sampling layer by layer or at an even closer spacing with longitudinal halving of the core samples, the low amount necessary to examining thin sections, volume weight, specific weight, diatom content, palynological and granulometric determinations, was separated and the rest ground to homogenize the samples for derivatographic and spectral analyses, Fischer's analysis method and other carbon-chemical tests, further on, for ash-content, carbonate and Ca—Mg content determinations. In view of its usefulness, Fischer's analysis, the carbon-chemical tests and volume weight determinations are of crucial importance. Without these data the quality and quantity of the raw material are indeterminable. Some other tests are necessary to enable further research concerning the oil-shale.

a) Analyses by derivatograph (M. FÖLDVÁRI) serve to demonstrate the presence of raw material difficult to observe by the naked eye. Thus, with its aid the whole organic matter, burning at 380—600 °C if organically bound, could be determined with relative precision. In the case of borehole Put-3, this is conform to the expectance, a quantity far over the sedimantary average. Taking into consideration 36 analyses, the value of each case surpassed 5 weight per cent, only in 3 cases was the value between 5 and 15 per cent. The results were as follows: in the subdivision from 38.4 to 20.0 m 22—25%, from 20.0 to 12.0 m 32—72%, and from 12.0 to 1.0 m 5—22%.

Raw material content determined by derivatograph may roughly correlate with the combustion value of oil-shale, its bitumen, volatile and hydrogen content, suggesting thus their close relationship. It is, however, striking, that the above-mentioned correlation is only approximate, in many cases being unambiguous. Thus on the basis of organic matter content the included volatile and bitumen can be determined only with a considerable error.

A significant difference presents itself in the organic matter to bitumen ratio between the Pula and Gérce sections. At Pula in 30% organic matter 4—8% is bitumen, and in 35—70% organic matter, the share of bitumen is 13—25%; while at Gérce the 25% organic matter contains only 1.2—5.5% bitumen. In both sections the organic matter content of the upper and lower part showed an identical character while in the middle part the organic content was less. The section of Gérce was even in this regard more homogeneous. These variations at Pula attain 12 to 70%, and at Gérce 3 to 35%. The differences of organic matter to bitumen ratio in oil-shale could be explained in both cases, at Pula and at Gérce, by the lack of accuracy in bitumen determinations or by the character of the organic substance. In any case, further studies are needed.

b) Under the term *qualification analyses* (P. TAKÁCS, MRS. ARATÓ, MRS. BELLA, MRS. KOVATSITS) the results of determinations of bitumen content, calorimeter tests, volatile content, humidity, sulphur and hydrogen content, and volume weight have been summarized.

The bitumen content of the above rocks was determined by the experts of the Mining Research Institute, taking as a basis the Hungarian standard obtained by Fischer's method. According to their data gained of samples taken layer by layer and then longitudinally halved, crushed and averaged, the bitumen content in borehole Put-3 (from 6.0 to 37.5 m) was 9.9—27.2 weight %, while in the section of Gérce (from 7.0 to 76.0 m), the weight per cent fluctuated between 1.2—8.4. The organic matter content of the upper and lower part in both sections contains significantly lesser bitumen as the middle part. The frequency of green laminae in the section of Pula, seen even by naked eye, is in close connection with the higher amount of bitumen. At Gérce both the green and red-brown laminae contain bitumen, and even in the dolomite marls of the upper part a considerable amount of bitumen is present. It may be remarked that, nearly half of the organic matter can be dissolved in a bensene-alcoholic substance. Thus it can be processed even in this way, provided that a greater part of the economically useful organic material disappears.

The volatile content shows a rough correlation with the quantity of bitumen: its amount in the section of Pula approximates 30%, while in the section of Gérce this figure is about 20%.

A similar trend was shown in both sections by the ash content of the rocks. In the case of Pula, when burning out occurs about 1000 °C, this value attains 65%; however, in the middle part of the section with higher bitumen content, it is only 40—50%. At Gérce, when the ignition is carried out at about 600 °C, this value attains 80%, and never decreases below 70%.

Moisture in both sections is about 7% and while at Gérce it scarcely changes, at Pula it shows significant variations.

Calorimetric value was determined only for samples of Pula. It presented along the section a very similar curve as that of the bitumen content with a value variation from 120 to 3350 kg/cal.

Very close connection with the calorimetric value, even a function of it, manifests the extremely high hydrogen content of the rock, changing along the section from 0.75 to 5.4%. A critical point for every fuel material is the sulphur content. The quality of oil-shales of Pula and Gérce is also in this regard very favourable with the low sulphur content, the amount of which decreases step by step: from 1.1 to 0.1 at Pula and from 0.9 to 0.1 at Gérce, respectively. It may be remarked, however, that the sulphur content shows no correlation with the ash or the volatile content. At the same time it changes parallel to the frequency of diatoms and the quantity of carbo-

nate. The 0.1—1.1% sulphur content for oil-shales is strikingly low. According to H. FÜCHTBAUER and G. MÜLLER (1970), bituminous shales contain 3 to 20% pyrite (in average 8.2%), which would mean roughly 1.6—11.0% (that is 4.2%) sulphur content.

The distillation refinery gas yield of Pula was measured, too, from samples taken werhe the oil-shale was most abundant (6.0 to 18.0 m). The sample yielded 54.0 m^3 gas/ton, from which 13 volume weight per cent is CO_2+H_2S, 4 volume weight per cent is CO, 8 volume weight percent O_2 and the rest (75%) other materials (hydrocarbons). At Gérce such studies were not carried out.

Volume weight determinations are indispensable for the estimation of resources. The analyses were processed by mercurial method (G. SOLTI). In the section of Pula (6 to 20 m), apparently of highest practical value, the volume weight, according to expectations, is very low (0.80—1.14 kg/litre). The lowest values occurred in alginite and in the layers of higher organic content. Except for the 50 cm thick dolomitic silstone, the average value attained 0.95 kg/litre (thus at calculations, practically, it may be reckoned with 1 volume weight). The specific weight of rocks from Pula varies between 2.45 and 1.15 g/cm^3. There is a close connection between organic matter content and specific weight, which is evident if we take into consideration the specific weight conditions of silicate and organogenic minerals.

At Gérce, because of the higher ash content, even the volume weight data were higher: varying from 0.61 to 1.42 kg/litre in the 15.4 and 76.0 m interval and with an average value of 1.1 kg/litre, which is remarkably low when compared to the average of the Pannonian clay marl (1.8—2.2) or lignite (1.20 kg/litre). Obviously, the majority of the minute *Botryococcus* colonies is not filled with mineral pelites, hence the marked looseness of the rock.

Summing up the results of the above testing of materials, it may be concluded that, thebasalts or basalt tuffs in the sections of Pula and Gérce, are overlain by a formation (40—38.4 m that is, 7.0—76.0 m respectively) practically representing a kind of oil-shale. The oil-shale of Gérce is of lower quality while that of Pula is somewhat better, being of higher quality in the 6.0 to 18.0 m interval and reaching a "very high quality" in the 15.0 to 18.0 m one.

c) It should be mentioned here, that because of the presence of a particular facies, the two sections were subject to *spectral analyses*. According to P. ZENTAI, there were no striking values. Table 2 presents the extreme and average values.

d) For the purpose of *petrographic* characterization granulometric composition and calcite-dolomite ratio determinations were carried out, layer by layer, of the oil-shale sequences of Pula and Gérce. According to these, significant differences between the two series were revealed.

Taking into account the granulometric composition it may be stated that the clay content of borehole Put-3 varies from 14 to 60%. Below 18 m depth the share of the clay fraction shows an increasing trend, then, at 18 m, a sudden decline is observed to be followed further up, again, by an increase with significant fluctuations. In the 6 to 18 m interval more abundant in organic matter, the sand fraction was also considerably represented, though the sand grains themselves could not be observed in the rock. This may be due to coagulation of the organic matter. In fact, the rocks are made up mostly of siltstone fraction, which can be observed even by unaided eye.

The section of Gérce is characterized by higher ratio of the siltstone fraction. In the 20 to 60% interval the clay fraction increases up to 42 m (on the average it is about 40%). At this height it significantly declines but increases again up to the top.

TABLE 2

Trace element content in ppm, of the ash recovered from 19 samples of the 4.0—38.4 m interval, borehole Put-3, Pula, after ignition at 600 °C

	Elements														
Values	B	Mn	Cu	Pb	Ga	Mo	V	Ti	Zn	Ni	Co	Sr	Cr	Ba	Li
Highest	160	4000	250	40	16	100	400	10 000	160	160	60	1000	160	1600	250
Average	85	2294	128	17	9	33	159	3 484	112	80	29	831	78	753	131
Lowest	40	1000	60	6	2.5	<6	40	400	40	40	10	600	40	250	60

Trace element content in ppm, of the ash recovered from 49 samples of the 6.4—90.6 m interval of borehole Gát-1, Gérce, after ignition at 600 °C

	Elements														
Values	B	Mn	Cu	Pb	Ga	Mo	V	Ti	Zn	Ni	Co	Sr	Cr	Ba	Li
Highest	400	2500	150	60	60	100	250	10 000	250	250	60	1600	400	2500	6
Average	194	1622	67	22	30	12	105	7 367	70	104	24	813	146	922	6
Lowest	60	600	25	4	10	10	40	1 000	<160	16	10	60	40	400	6

The rest of the sediments is made up of siltstone; sand fraction in turn occurs only in some layers reaching a maximum of 5%.

The calcite content of the sediments at Pula show upward significant variations in the profile, decreasing from 63% to 23% and showing then a sudden increase in the final bed. At the same time, the dolomite content is about 5% up to the end, except for an increase to 8—21% in the organically enriched part of the profile where it becomes occasionally even predominant. In the final part, i. e. the calcareous marl sequence, the quantity of dolomite is significantly higher than that of calcite. Thus, the share of dolomite shows a gradual increase upward.

In the section of Gérce, the calcite content of the sediments varies between 15 and 26%, however, unlike at Pula, it shows a slightly increasing trend. The dolomite content varies between 3 and 18%, its ratio increases and from 54 m on, it gets in equilibrium with calcite. Thus the two sections show similar development. The most logical interpretation accounting for the difference in calcite content between the sequence of Pula and that of Gérce is to suppose that Pula must have had a calcium carbonate environment.

6. PALEONTOLOGICAL INVESTIGATION

Paleontological research had two aims. First, the age of sediments overlying the basalt had to be determined. This was all the more important, as no sediment was found in the immediate hanging wall of the Transdanubian basalt or in their closest vicinity and, therefore, the basalts were declared, on and on, to be partly or totally of Pleistocene age.

The other task was to determine the facies. M. HAJÓS identified 1—52 diatom species in various samples of the sequence. The number of species and also their frequency show an upward decrease. (This has been expressed with so-called frequency show an upward decrease. (This has been expressed with so-called frequency indices: "sparse"=1, "fair"=2, "frequent"=3, "abundant"=4.) As was mentioned above, pyrite, sulphur and carbonate presents a decrease with the reduction of the amount of diatoms, while dolomite increases with decreasing diatom content. The abundance of the diatomaceous microflora is an evidence of favourable life-conditions, the sufficiency of oxygen, insolation and mineral nutrients. Since the combustible organic matter content increases rather inversely to the content of diatoms, it is very possible that the conditions for the life of planktonic diatoms became, with the passing of time, more and more unfavourable, while *Botryococcus* were to find gradually more favourable conditions of living.

The diatomaceous flora proves impressively the presence of the Upper Pannonian. This statement, however, relies on paleoclimatic and water quality considerations rather than on biostratigraphic results. On the basis of the ranges of the species identified, the rocks may be both older or even younger, that is, of Pleistocene age. The microflora testifies to a rather warm February water temperature: 11 °C, slightly brackish water. The two phenomena combined could hardly occur in Pleistocene time.

According to E. NAGY, the palynological aspect of the samples from boreholes Put-1, Put-3 and Gét-1 shows a typical Pannonian floral assemblage. One of the most characteristic forms of this assemblage is the planktonic alga *Botryococcus braunii* KÜTZ., one of the main constituent of bituminite-rich solid rock. Besides the pelagic Botryococcus, the most significant role was played by the representatives of *Conifera* family (*Abies, Tsuga, Cedrus* etc.). Their presence suggests the one-time occurrence of Mediterranean-type coniferous forests in the closest or wider neigh-

bourhood. At altitudes below those of the coniferous vegetation, there was a habitat composed of deciduous trees again of Mediterranean type (*Celtis, Carpinus, Zelkova, Ulmus, Juglans, Betula, Fagus, Quercus, Acer, Ilex, Liquidambar)*. The presence of swamp forests on the shore of the Pannonian lake is evidenced by the genera *Nyssa, Taxodium, Alnus, Carya, Pterocarya.* Accordingly, the vegetation of the neighbourhood testifies to a humid climate warmer than present-day's, i. e. to one of Pannonian rather than Pleistocene type.

According to I. PÁLFALVY, the microflora is mostly represented by sedges, though Upper Pannonian deciduous trees *(Liquidambar, Quercus)* also occur.

A rather great number of well-preserved remnants of *Ostracoda* have been recovered from the lower beds of both sections. On the basis of a sample from borehole Put-3, M. SZÉLES determined a typical Upper Pannonian, slightly brackish water, fauna.

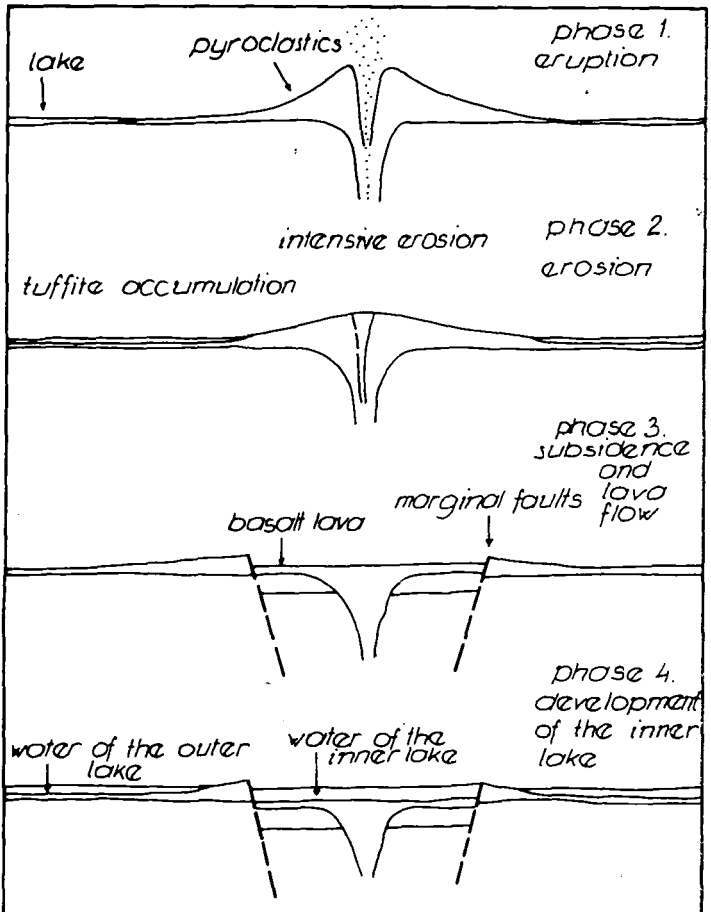
Again from borehole Put-3 (32.4 and 35.4 m) mollusc fragments have been recovered. These were determined by E. KROLOPP as *Radix aff. peregra* (MÜLL.), living in a freshwater environment, but occurring in both the Pannonian and Pleistocene rocks. *Pisidium sp.* from 32.4 m lived in fresh or slightly brackish water.

Summarizing the above, it may be concluded that the paleontological character of the alginite sequence overlying the basalt is closely connected with that of Upper Pannonian formation, though it does not contain any fossil enabling a firm chronostratigraphic assignment either to the Pliocene or the Pleistocene.

7. PALEOGEOGRAPHY AND GEOHISTORY

At the end of the middle Upper Pannonian, the area — taken *in sensu lato* — was covered by a system basalt tuffites a few metre to tens of metres thick. It is only around the eruption centres overlying the cross-laminated beds that true continental (that is, air-borne) basalt tuffs and agglomerate layer can be found and the first basalt lava bed is even more delimited *(Fig. 5)*. In most cases the first basalt tuff layer is present now only there, where during the Pannonian and the Pleistocene it was protected from weathering by the hard bed of first basalt lava flow. The first eruption cycle was soon followed by a second one, sometimes with quite new eruption centres as that of Pula and, as shown by analogy, that of Gérce as well. This eruption cycle consisted of a single intensive ejection, during which at the eruptive centre first a low volcanic cone was formed, then in the second phase, after the appearance of the basalt lava, the middle part of the original volcanic cone subsided along volcanotectonic fractures and its base was filled up with basalt lava. In the third phase of development, as a consequence of the continuous subsidence during the development of Upper Pannonian formation, lacustrine water intruded through the lithoclases of the tuff ring or through some channels above the more shallow parts, into the cooled volcanic body. Here, despite of shallow lakes of varying size becoming repeatedly swampy and extending over the whole Tapolca—Nagyvázsony basin. The quiet and low sedimentation was disturbed by basalt eruptions along deep fracture lines presently unknown. Although it is very unusual but it can be taken as a fact, that sedimentation was influenced by these eruptions only over a very limited area. The pyroclastic material of basalt reaching to the surface with the beginning of the first eruption was absorbed by the Upper Pannonian lake system. While over an area of several km^2 inwashed water-fallen tuffs few occurred, the positive volcanic forms — if any — were limited only to a few thousand m^2, i. e. very small areas. The thin tuff layers of inwashed or water-fallen origin were argillized

Fig. 5.



Stages of the Transdanubian basalt eruptions which developed the structure of the oil-shale holder

under the water or partly above it; in fact, minor waves could sweep tuffs away to great distances within the lake system letting them completely disappear.

In the second part of the eruption, a significant volume of pyroclastics reached to the surface, and built up a volcanic cone arising above the lake. Simultaneously with eruptions torrents swept slurry flows from the mountains to the surface of the Pannonian lacustrine sediments, forming in the territory of the Balaton Highland arched cross-laminated the isolation, the rather significantly deep (5—10 m) water and average Upper Pannonian conditions, the intensive near-by weathering of basalt tuff glass resulted in abundance of nutrients, forming special sedimentation conditions. The low hydrodynamics of the Upper Pannonian lake was not able, or was so only in a very limited form, to transport the fine pelitic material and into the inner lake, thus the pelite mainly originated from the eroded inner side of the basalt ring (at Gérce locally reaching even a grain size of sand) of which the filling material is made up. Besides a significant quantity of calcipelite (precipitated as a result of the general bacterial activities), subdued dolopelite, further on perished planktonic algae — in the beginning with diatoms, later mainly Botryococcus forms — were added. The ratio of the three main components changed — on the basis of the size of lamination — according to seasons being a function of the insolation, distribution of precipitation and quantity of available nutrients. At present it is not known, which season is represented by the 0.1—5.0—mm-thick laminae of different composition. Obviously those rich in lime manifest the warm summer time. Considering the average thickness of laminae being 0.5 mm, the sequence at Pula may be of 50,000 years and at Gérce of 140,000 years.

Taking into consideration the increasing amount of dolomite material and desiccation structures within the section of Pula, the crater lakes showed a trend of drying out. In the rather deep water of the lake, protected from wind, the original lamination of the sediments was preserved under the water table covered by algal cultures (*Botryococcus* colonies). Under such conditions, the rolling waves could not develop their stirring and resedimenting influence. The effect of the rather steep immediate neighbourhood of great relative relief is not manifested well enough in the sediments. This may be due to the filter effect of the dense vegetation of sedge and reed (*Taxodium* etc.) in the shallow water along the shore of the lake, though it is abvious that several years after cooling out of the crater, its inner side was covered by a dense vegetation which impeded in a similar way the getting in of coarse material. In spite of this, the life of crater lakes was not completely undisturbed. Slumping activities took place periodically, mainly as a consequence of earthquakes related to volcanism.

The macrofauna is lacking in both series studied at Pula and Gérce, moreover those debris found in the section of Pula are of freshwater origin, which is not in agreement with the determinations concerning the "slightly brackish environment" of the diatom flora. The lack of brackish water molluscan fauna has to be interpreted by a special anaerobic bottom mud, while some freshwater debris could be introduced by nektoplanktonic transportation afloat.

Attention has to be called to the fact that the alginitic rocks cannot be fitted in the swampy zone system of coal-formation, which means that a deep origin can be proved only for some types. Theoretically, a mud with abundant algae, combustible in dry state, bearing much bituminite and with few other sediments may be deposited in a closed water where there is no sediment transportation and the accumulated material was affected by diagenetic processes under anaerobic circumstances and thus its organic content is not subjected to oxidation. The extension of bituminite-

rich oil-shale formations as well, as several examples of other countries manifest this unanimously in Hungary. (BRADLEY, W. H., 1964, 1970; CANE, R. F., 1969; DUNCAN, D. C. and SWANSON, V. E., 1965; MÜLLER, G. and BLASCHKE, R., 1969).

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NEOGENE EVOLUTION OF THE SOUTHEASTERN PART OF THE GREAT HUNGARIAN PLAIN ON THE BASIS OF SEDIMENTOLOGICAL INVESTIGATIONS

M. MUCSI AND I. RÉVÉSZ

ABSTRACT

The aspect and opinion of authors on the Neogene of the southeastern Great Plain were established as a result of the elaboration and sedimentological investigation of about 10 000 core samples. In addition to the structural and textural features of the rock samples the structural situation within the basin, as well as certain geochemical peculiarities and paleogeomorphological relations were also taken into consideration. The rhythmicity occurring in the Neogene sediment accumulations as well as the structural features of this rhythmicity were regarded significant factors. The study draws conclusions on the paleogeographic environment and modes of sedimentation.

INTRODUCTION

The area investigated lies in the southeastern part of Hungary. The majority of the detailed data published in this paper concerns the Pliocene sediments of the close vicinity of Szeged. In this part of the Neogene geosyncline of the Great Plain varied rock formations and facies were observed. Together with the sequence of 100 to 250 metres thickness which can be assigned to the Quaternary, the total thickness of the Neogene varies between 1000 and 6000 metres; in a smaller part of the area a value greater than 6000 metres can also be assumed.

Numerous geologists and paleontologists dealt with the filling up of the Carpathian Basin during the Neogene. Their statements can be comprehensively assigned to two directions. The first group of great number supposes erosion between the single stages and denies the continuous sedimentation. This direction was founded by M. HOERNESS [1853—1867] and KARRER [1877]. Others, the followers of HALAVÁTS [1882—1923] and LÓCZY [1913] assume continuous sedimentation.

The researchers of our days insist also on contradictory statements with compromises corresponding to the local features of the investigated basin part. On the basis of the borehole data it becomes ever conspicuous that the central formations of the basin cannot be or can be only conditionally identified with those of the marginal part or of central mountains type. The latter ones were several times studied both in superficial outcrops and in boreholes. The researchers assuming discordances start from these near-shore, thin strata and make generalization on the central part, too.

The most up-to-date and detailed investigations showed, however, the continuous sedimentation in relation with the marginal parts; in the strata sequence of concordant stratification tuff spreading indicates the boundary between Miocene and Pliocene [JÁMBOR, Á., 1971].

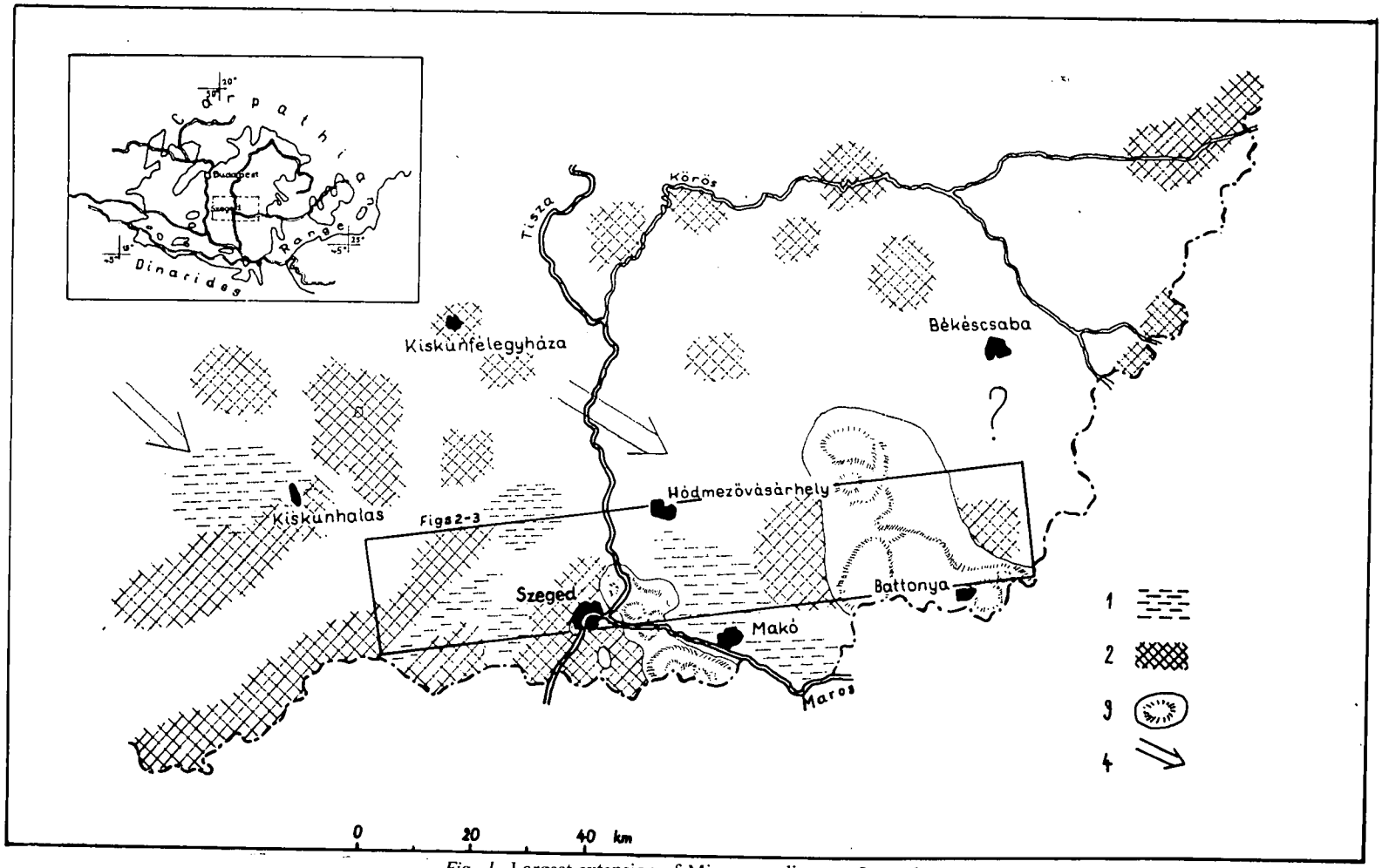

Fig. 1. Largest extension of Miocene sediments. Legend:
1) Miocene sediments accumulated at considerable water depth, in a reductive environment; *2)* Upper Miocene shallow water, saline or brackish water environment with islands of small area; *3)* Land em g g t iocene; *4)* Direction of transgression

GENERAL STRATIGRAPHY

Basement

In the floor of the Neogene ("basement") sediments of varied facies are known [SZEPESHÁZY, K., 1973 and 1974]. On the basis of data obtained till now it can be assumed that among the basement formations the metamorphic schists and mesothermal gneisses, which can be assigned to the Precambrian, predominate. The rocks of Permian to Lower Cretaceous ages are also frequent, out of them the Triassic dolomites seem to be the most wide-spread ones. In the basement palingenic granites, granodiorites and quartzporphyres are also known; the latter one is hardly identified since the boreholes did not traverse volcanic sequence everywhere.

From the Upper Cretaceous to the Miocene, as well as in smaller spots to the Pliocene a long-lasting and intense erosion phase can be taken into account. The eroded sedimentary mass accumulated in the Carpathian flysch zones and in the Intra-Carpathian Paleogene troughs. Authors agree with the opinion that the recent spatial position of the rocks of different age and quality of the basement considerably differs from the original one, also in horizontal sense [SZEPESHÁZY, K. 1973].

Neogene sequence

The priority of chronostratigraphic classification was accepted as theoretical basis as against the biostratigraphic classification [HORUSITZKY, F., 1955 and 1971]. The Miocene, Pliocene and Quaternary strata of the investigated area belong to one structural stage. The temporal boundaries of the Neogene stages and parts of Hungary are recently only imagined isochronous surfaces. Errors are caused by the fact that limiting space of time has been attributed by researchers to lithological units and strata groups, or to certain fossils.

It is a fact that all the details of geological interpretation are interwoven by hypotheses. Some of the investigations are numeric and concrete but by the time one reaches the past by conclusions, i. e. from a past into another, from one field to the other it should be accepted that there is high probability of error. The ideal or required aim is to determine the formations of the geological past at a given moment. The geologists should be the geomorphologist, biologist and chemist of the past to realize this aim. The fact that the researchers of the earth sciences make bold to publish against of the aforementioned is due to their optimism and beside it that many hypotheses are proved by the ever increasing amount of industrial, mining experiences.

The mode, rate and environmental aspects of filling up as well as the paleobiocoenoses are known from several concepts but the dialectic aspect is missing in them.

Miocene

The Neogene sequence of strata of the South Great Plain shows continuous sedimentation and the unconformities caused by facies differences does not mean the interruption of continuity but indicates the spatial and temporal replacements of these facies [MUCSI, 1973].

As a result of the Styrian orogeny trench-like subsidences were originated also in the area of the South Great Plain. This phase shows a few and uncertain informations since the locations of the first Miocene transgressions fall also recently into

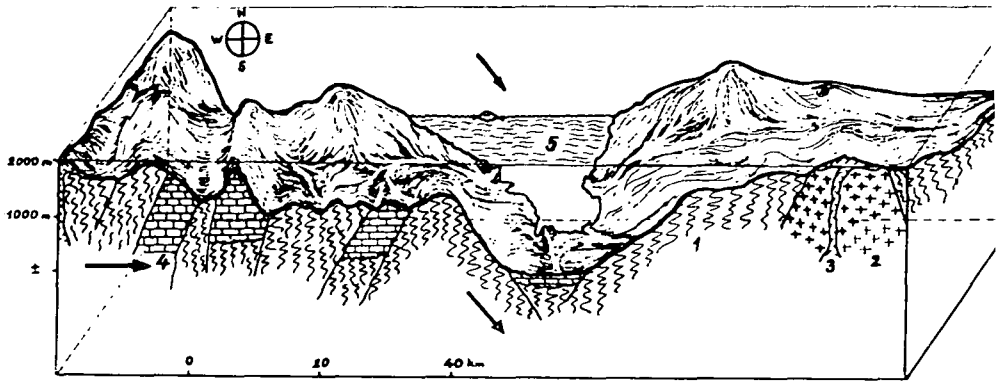

Fig. 2. Schematic block diagram showing the beginning of Miocene transgression. Basements: *1.* Metamorphic, *2.* Granitic, *3.* Quartz porphyric, *4.* Sedimentary, *5.* Sea

the structurally deep zones and these are hardly discovered by drills *(Fig. 2)*. Helvetian formations are known from the vicinity of Kiskunhalas, their presence, however, can be rendered probable also at other locations (*e. g.* the depression of Hódmező-vásárhely).

In the Carpathian Basin the climax of Neogene transgression followed within the Tortonian (*Figs. 1* and *3*). The complete Tortonian strata sequences of greatest thickness are found also in the areas of relatively deeper structural position. The depression southwest of Kiskunhalas is an exception where as against the thickness of 2000 metres of the Miocene sequence, the Pliocene hardly surpasses the thickness of 1000 metres. The rock material is of varied quality and extends from the near-shore conglomerates to the pyritic pelites accumulated in reductive medium and to the carbonates, respectively. The flysch-type sediment of the formerly and recently deep-seated areas is also worthy of mention. The accumulation of the sediments of coarser grain size took probably place from turbidity currents. At their recent place these are "foreign rocks" and faciologically dissimilar. During the Tortonian the multiphase crustal movements, the related earthquakes and the inclination of the sea-floor generated these sediment "clouds". The intermediary period is characterized first of all by the change of pH, further by other changes, e. g. salinity etc. as a function of which clay-marl ($CaCO_3$: 10 to 40 per cent), marl ($CaCO_3$: 40 to 60 per cent), lime-marl ($CaCO_3$: more than 60 per cent) were formed.

During the Sarmatian — regarding its absolute space of time — continuous sedimentation is assumed in the area in question. The Tortonian — Sarmatian boundary, resp. the connection of the two stages could not be fixed. In the area of the Great Plain the assignment to Sarmatian is carried out on the basis of hydrocarbon exploring borings first of all by fauna impoverishment relating to limnification. Consequently, in the central part of the basin its space of time is the absolute time of the Tortonian-Pliocene freshening [MUCSI, M., 1973] which depends on the fundamentals of the localities.

The maps demonstrating the distribution of seas and continents within the Miocene [HÁMOR, G., JÁMBOR, Á., 1971; JÁMBOR, Á., 1971] show that the "assumed extension of the Sarmatian marine formations" was greater than the whole area

of the "Tortonian pelagic and littoral" formations. Areal displacements are taken into account also by the authors mentioned above.

According to MERKLIN, R. L. [1959] the Sarmatian of Hungary corresponds to the Upper and partly to the Middle Lower Sarmatian known from the southern areas of the Soviet Union. The other parts of Miocene are represented in Hungary by Pannonian facies. JÁMBOR, Á. [1971] renders the Sarmatian time of Hungary between the Upper Badenian (Upper Tortonian) and the Lower Pannonian (about the Lower Pliocene) and fixes its stratigraphic boundaries by changes in the bio- and lithofacies.

As to our opinion the investigated area has continuously subsided with changing intensity and proved to be a geosyncline till the Recent getting a deeper position as compared to its environment. Relative "pseudo-uplift" resulted in by filling-up of local significance is possible. In the Carpathian Basin the rise of Central Mountains resulted in enviroments dissimilar of that of the South Great Plain. Thus, in the central part of the geosyncline the research of the litho- and biofacies corresponding to the classical, evaluated sequences of Central Mountain type becomes resultless. The statement that the lack of marginal facies means erosion periods and uplift is believed causeless. This is especially unacceptable since the lack of Sarmatian facies is apparent and these are supposed to be in the deep zones.

In the area of the South Great Plain hiatus, especially erosion, denudation cannot be evidenced at the Tortonian—Sarmatian—Pliocene boundaries on a stratigraphic basis (photos from the bores of Makó and Hódmezővásárhely, probably those of Forráskút, Sándorfalva). In Hungary the strating sediments of the Lower Pannonian (Lower Pliocene) are assigned to the Sarmatian interval without indicating the Miocene-Pliocene time horizon based on absolute age within this sequence. The Miocene-Pliocene boundary fixed earlier was dated by the appearance of *Limnocardium* and *Congeria* and by the disappearance of foraminifers. This is, however, only the change of biofacies and does not mean the change of the lithofacies, as well.

In the area of the South Great Plain the Miocene-Pliocene boundary is marked by the change in the chemical composition of the geosyncline's water which was manifested in a long-lasting freshening process. In several western, northern, eastern and southern units of the Carpathian Basin (*e. g.* Nógrád Basin, Sopron environs,

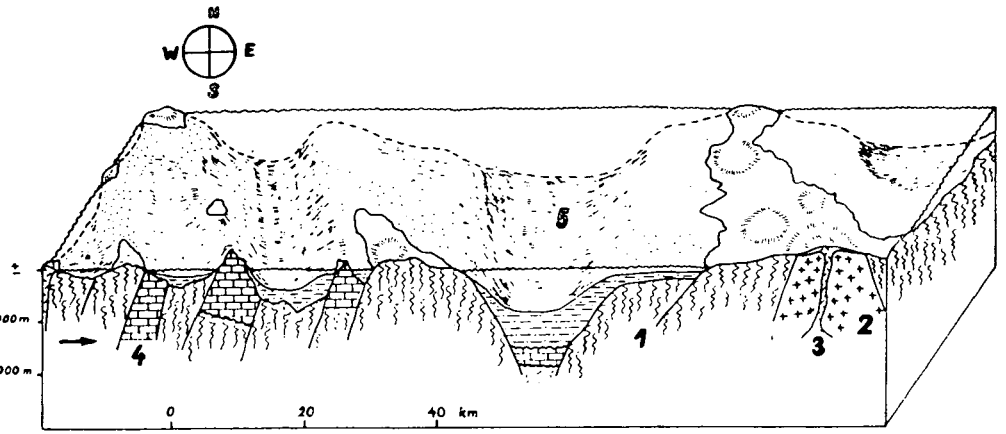

Fig. 3. Diagrammatic representation of the beginning of Lower Pannonian. Legend, see Fig. 2.

Transylvania, etc.) the Neogene cycle was completed by the Miocene. This regression process is reflected only by freshening in the investigated area. The islands, peninsulae shown in *Fig. 3* were inundated, consequently the Pliocene formations surpass here those of Miocene age, at the same time regarding the whole of the Carpathian Basin the regression filling-up mechanism becomes predominant. This phenomenon and high-grade change in the connection between the Carpathian and Pontian-Caspian basin are responsible for the differences of strata sequences and differences of time intervals of Hungary and of the neighbouring countries.

A further significant change is that with gradual rising of the Alps and Carpathians the drainage basin of the Pannonian Basin has considerably increased. Its water budget showed a positive trend as a result of these processes [JÁMBOR, 1971]. The inland sea transformed into an inland lake and its water surplus was drained towards the Rumanian Plain through channel-like ways.

As to our experiences the Miocene-Pliocene boundary can be marked by the disappearance of the gravel beds connected to turbidite currents in the internal and deep basin parts and by that of the only "gravel coats" at the boundary. The whole thickness of the Miocene sequence is characterized by the presence of conglomerate, sandstone, aleurolite, clay-marl, marl and lime-marl. Regarding their origin these rocks are developed partly in turbidite currents and partly in undisturbed water. The two genetic types form "half-rhythms" and the thickness of these is strongly changing. Generally and first of all at the end of Miocene the pelitic-calcareous phases predominate.

The thinning out resp. disappearance of the gravelly strata follows within a section of about 200 metres length *e. g.* in the Hódmezővásárhely depression; this section contains both foraminifers and *Limnocardium* (very small and only impressions). On the basis of *Limnocardium* this section is considered to be Pliocene.

Within the investigated basin part in the region of relative rises, occasionally islands and peninsulae the near-shore litho- and biofacies are characteristic. In many cases these are similar to the marginal formations.

Pliocene

Out of the oldest Pliocene formations the coarse clastics are connected to the islands of the Miocene inland sea. Depending on the facies the conglomerate, sandstone, aleurolite, clay-marl or carbonate sediments are known close to each other in space (Algyő, Sándorfalva, Forráskút, Szeged, Makó, Hódmezővásárhely, Fábiánsebestyén). Post-Miocene erosion should be taken into account at the places where formerly the sedimentation has not started.

In the investigated area numerous bores traversed the Pliocene "basal conglomerate". On the basis of its grain-size composition* this formation is mostly gravelly coarse-grained and medium-grained sandstone and reaches only rarely (the lowest several metres of the sequence) the conglomerate grain-size composition. Small quantity of very fine and fine grained sandstone also occurs in the sequence by means of which the apparently uniform rhythm can be divided into sub-rhythms. In the single sub-rhythms, but tendentiously in the whole "conglomerate" sequence the upward refinement of grain-size composition can be fixed. Classification becomes locally easier by means of the hard impermeable intercalations of calcareous cementing material. In the arrangement of the gravel substance of 1 to 40 weight per cent no orientation can be observed. The elements of stratification can be hard-

ly observed, almost all the boundary surfaces are indistinct and gradual. This phenomenon is considered one of the significant evidences of the accumulation in the surf zone. In the bores located into the deeper structural position the refinement of grain-size composition as well as the decrease of the quantity of gravel fraction can be observed. When approaching the top of the horizon similar material change can be observed which proves the increase of distance from the shores of the accumulation and the changing conditions of the kinetic energy. The NaCl content of the waters deriving from this sequence changes between 10 and 15 mg/l. Lime-marl is the overlying layer and since it is tectonically undisturbed it can be assumed that this value is similar to the original salt concentration of the Lower Pannonian inland lake. When a dilution of small measure is accepted, the real value was certainly around the upper limit or slightly surpassed it.

The conglomerate is overlain by the "lime-marl horizon" containing pyritized plant remnants, bacteriopyrite and pyrite concretions and calciumcarbonate consisting of microcrystals in 60 to 95 per cent. The preceding clastic layer is separated by this phase of transitional material (fine sandstone, calcareous fine sandstone, limy aleurolite, marl) the thickness of which is mostly 1 to 2 metres. In the deepening parts of the basin, however, this transitional member may become thicker and there it can be divided into sub-rhythms of straight classification (their number does not exceed 10). The mode of deposition and the textural features relate to accumulation from turbidite currents. The formation of turbidite currents was resulted in by the floor relief though in this case only a displacement of several kilometres comes into question.

The clastic horizon occurs only in connection with the relative emergences of the basement, but the lime-marl is already a wide-spread sediment in the areas of the South Great Plain explored till now. Where the Neogene is of small thickness (Ásotthalom, Kelebia, Battonya, Mezőhegyes) it is not necessarily of open water and deep water facies, its color is virtually light-yellow. Regarding the whole investigated area its heteropic facies were observed only in several cases (Algyő, Ferencszállás). In the areas of deep structural position (Makó—Hódmezővásárhely trench, Békés-depression, Dorozsma—Kistelek trench) the marls and lime-marls with bacteriopyrite, pyritized plant remnants and of blackish-grey color are considered the oldest Lower Pannonian sediments. These were formed in deep water and euxinic environments. Summing up, the lime-marl is a chemical sediment both in the shallow, in the deep and in the medium areas but the reductive conditions can be assumed only in case of the two latter ones.

The two strata are called together Pliocene basal horizon though in the investi-

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* Grain size limits used in this study:	∅ mm
conglomerate (gravel) in general	2—200
fine-grained conglomerate	2—5
sand, in general	0.06—2
coarse-grained sand	0.5 —2
medium-grained sand	0.2 —0.5
fine-grained sand	0.1 —0.2
very fine-grained sand	0.06 —0.1
aleurolite, in general	0.005—0.06
coarse-grained aleurolite	0.02 —0.06
fine-grained aleurolite	0.005—0.02
clay, in general	below 0.005
fine clay	below 0.002

gated area of 10 000 km² their joint occurrence can be observed only in special cases, i.e. in connection with the greater emergences of the basement. The totla thickness is strongly varying, it extends from several metres to hundred metres.

This Pannonian formations being considered the oldest ones is overlain by a Lower Pannonian sequence of 200 to 2 800 metres thickness. Coarser fractions do not occur (grain diameter of 1 mm only in case of micas). It rarely contains lime-marl and marl intercalations, their thickness amounts to 20 to 30 cm at most.

On the basis of the texture, structure and quality of the rock material the following types are distinguished:

"A" It is of clay-marl and fine aleurolite material, unstratified or hardly stratified. The "rolling" clay-marl is frequent. The rock consists mainly of clay minerals with considerable chlorite and dolomite content.

"B" It consists of the alternation of fine and coarse aleurolite containing less fine sandstone beds (max. of several 10 cm thickness) and wedging lenses. Stratified. The "rolling" clay-marl occurs. The sandy phases may be of coalified plant remnants. The rock consists of clay minerals, chlorite, dolomite and quartz.

"C" Its material is fine and very fine sandstone containing less aleurolite and clay-marl intercalations and wedging lenses; it is stratified and often of coalified plant remnants (first of all the thin-bedded, fine-sandy parts).

"D" It contains unstratified of hardly stratified phases consisting of fine and very fine sandstone.

In the "Szeged Basin" and in the area of the depressions of relatively deep structural position the thickness of any types does not exceed 20 metres. These are mostly of several metres thickness. The grain-size composition shows refinement tendency from the top downward, or from down upward. These subunits of the sequence of 20 to 40 metres thickness can be divided into sub-rhythms almost without exception. (Their thickness is of metre of order.) The base rhythm and especially the sub-rhythms are of asymmetric structure.

Within the Lower Pannonian sequence of a research field 30 to 50 rhythms can be distinguished in the areas of medium-deep and deep structural position. The single rhythms consist of the A, B, C, D sediment types classified above being of varied sequence and thickness, their structure is often incomplete.

The limits of rhythms are drawn always in type "A" since the lime-marl horizon is overlain by clay-marl. The frequent rhythms-types of the strata sequences are as follows:

A B C D C B / A..	(occurs everywhere, one C or B may be absent)
A B C D / A..	(rather in the upper part, out of B C D anyone may be absent, but A D A never occurs)
A D C B / A..	(rather in the lower part, out of D C B anyone may be absent, but A D A never occurs)

To trace the spatial position of the rhythms is troublesome, their areal extension may amount to 100 km². The sandstones (D) are often wedging towards the relative emergences of the basment and become often clayey; it is probable that this occurs also towards the deeper parts. The ratio of the area of sandstones as compared to their thickness is very high, they seem to be of "sheet-type".

Within the types building up the rhythms on the basis of the changes of stratification and material quality further units, i.e. sub-rhythms can be distinguished. *E.g.* the type "A" is built up by the following variations:

"a_1" clay-marl, unstratified, rolling (in fresh air this decomposes within a few days to pieces of 0.5 to 2 cm diameter, of conchoidal-comminuted surface of elongated-flat shape; this fragmentation leads to the formation of pieces of millimetre diameter, apparently without any external influence);
"a_2" clay-marl, unstratified, banked structure;
"a_3" clay-marl of lamellar jointing (rare);
"a_4" rolling clay-marl with fine aleurolite intercalations;
"a_5" alternation of clay-marl and fine aleurolite, the clay-marl may be of rolling type, too;
"a_6" fine aleurolite with clay-marl intercalations, the clay-marl may be of rolling-type;
"a_7" fine aleurolite (often of lamellar jointing);
"a_8" fine aleurolite stratified with lamellae or lenses of millimetre thickness and of coarse aleurolite or fine sandstone material. These clastic sheets and lenses are always strongerly cemented.

The subdivision of the types "B" and "C" is based on similar principles but the number of variants is greater. Type "D" may be built up by the following variations:

"d_1" fine and very fine sandstone, unstratified;
"d_2" fine and very fine sandstone, stratified occasionally by mica and coalified clastic plant remnants;
"d_3" unstratified layers of fine and very fine sandstone of 1 to 50 cm thickness, always thin-lamellated and of lamellar formation, dissected by coarse and fine aleurolite intercalations;
"d_4" stratified layers of fine and very fine sandstone with mica, occasionally with coalified clastic plant remnants, thickness is 1 to 50 cm, always thin-lamellated and of lamellar formation; dissected by coarse and fine aleurolite intercalations;
"d_5" fine sandstone, stratified, contains occasionally coalified plant clastics; alternates with the layers of aleurolite and clay-marl of 1 to 50 cm thickness; the quantity of sandstone and pelites is nearly the same.

The sediments of the Lower Pannonian inland lake got their accumulation place either in floated or in dissolved state. The material transport within the basin was carried out by changing flows of mainly low energy level. In the core samples the directions of flows cannot be determined. Out of the factors relating to the sedimentation conditions the structural features appearing on the rocks are of special importance. In case of the Lower Pannonian sediments the features being assigned to the terms internal and external stratification and deformation structures are found in a wide range. Out of the internal stratification types some photos are demonstrated. The most important internal stratifications types are as follows:

horizontal, parallel lamination; and
varied sub-types of the complex stratification (horizontal, inclined, flaser, complex undulatory, interconnected and interrupted lense-like stratification).

Disregarding the base level these may occur everywhere. Out of the external or surficial features the mechanoglyphes are represented by flow features, the traces of objects are infrequent. Bioglyphes are frequent only in the upper part of the sequence. Deformation structures occur only locally.

The $CaCO_3$ content of the sediments is independent of the grain size composition, its average quantity amounts to about 30 per cent, the deviation is negligible

(20 to 45 per cent; number of measurements is about 1000). A few per cent of the carbonates is clastic, the overwhelming majority, however, is of syn- and epigenic origin. On the basis of the investigations of MEZŐSI, J. [1975] all the three types contain calcite and dolomite, but sulphates are absent.

Several hundred rock-physical investigations were carried out on sand sediments. The results of bulk density, porosity and permeability are shown in *Fig. 4*. It can be stated that in the Lower Pannonian sequence the bulk density results in an average of 2.2 g/cm^3 but in the upper section the values are smaller. The average of porosity is about 10 per cent, the greater values are infrequent. Permeability is consecutively very low, the most frequent values appear between 0.1 and 50 md; in this case the increase of the values in the upper part is also valid. The investigation results of a core sample of Lower Pannonian age are demonstrated in *Fig. 4*.

The salinity of the inland lake can only be estimated. From down to the top the total salt content changes tendentiously between 8 and 3 g/l. On the basis of the sporadically occurring shell fauna found in the clay-marls of the sequence and of theoretical geochemical considerations (*Limnocardium* and *Congeria,* resp. osmosis and ionfiltration), the original salt content was higher. As to our opinion this amounted to 15 to 20 g/l. As a result of investigations the quality of water is predominantly of NaCl.

It is problematic that in the South Great Plain the Lower Pannonian sequences of small thickness do not contain sandy intercalations but are built up practically without exception by clay-marl and fine aleurolite and only the sediments assigned to the type "A"/"a_s" represent the variety. On the contrary, in the parts of medium-deep and deep structural position only the rhythmic accumulation is characteristic, as described above. It seems to be the most simple explanation that these areas were ridges below the water table of the inland sea, probably in great distances from the shores, consequently from the flow zones of the deeper areas only the pelites and chemical sediments got these relative emergences. It is known that the flows on the bottom keep away from the relative emergences of the geosyncline's floor. The other reason may be the configuration of the water course network of the erosion area.

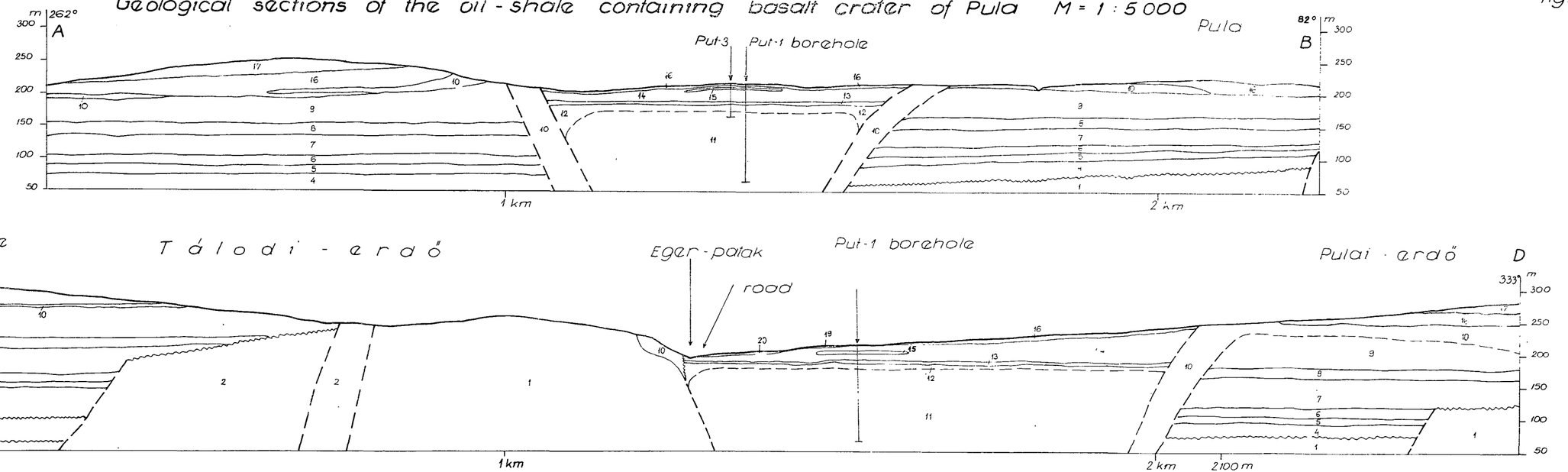
The investigation of the sedimentary features, the ratio of pelitic and psammitic sediments as well as of the vertical and horizontal connections of the core samples resulted in important paleogeographic conclusions.

The sediments were accumulated in the more distant and internal part of the basin parallel with the gradually increasing depth of water and growing distance from the shores. Flow and flow-free sediment types are distinguished. The latter one predominates in the shallow areas. The flow-free type is built up by clay-marls and fine aleurolites ("A"). All the other sediment types of the Lower Pannonian are more or less bound to flows.

In the medium-deep and deep structural areas, on the basis of the sedimentary features a deep and a shallow water sequence can be separated overlying temporally each other. The sandstones of the deep-water and older sequence are characterized especially by "clay-marl pebbles". These sediments may form as a results of subaquaeous avalanches. The avalanches are caused by the bottom relief and relate to contemporaneous shallow water environs. The steeper slopes are occasionally referred to by chaotically disturbed parts of the sequence. The differences of the bottom morphology being observable in the Lower Pannonian are partly inherited from the Miocene, and partly the results of the filling-up mechanism and gradual epirogenic subsidences renewing at the beginning of the Lower Pliocene. The considerable differences in depths of the geosyncline's bottom preserved also in the

Fig. 4.

Geological sections of the oil-shale containing basalt crater of Pula M = 1 : 5 000



Legend: 1. Upper Triassic, Hauptdolomit, 2. Carnian marl, limestone, 3. Middle Miocene, bauxitic clay, 4. Sarmatian limestone, marl, 5. Lower Pannonian marl, clay marl, 6. Upper Pannonian siltstone with Pectinidae, siltstone, quartz sand and freshwater limestone of Kapolcs, 7. Upper Pannonian clay marl, purple freshwater marl, coal-bearing clay, 8. Upper Pannonian clay, coal-bearing clay, 9. Upper Pannonian green clay, siltstone, 10. the 2nd basalt-tuff and bentonite, 11. the 2nd basalt, 12. Scoriaceous variant of the 2nd basalt, 13. Laminated siltstone, 14. Oil-shale member, 15. Calcareous dolomite, 16. Freshwater limestone of "Nagyvázsony" and marl, 17. the 3rd basalt-tuff, 18. the 3rd basalt, 19. Early Pleistocene terrace gravel, 20. Holocene terrace gravel, ~~~ Surface of unconformity / structural contour

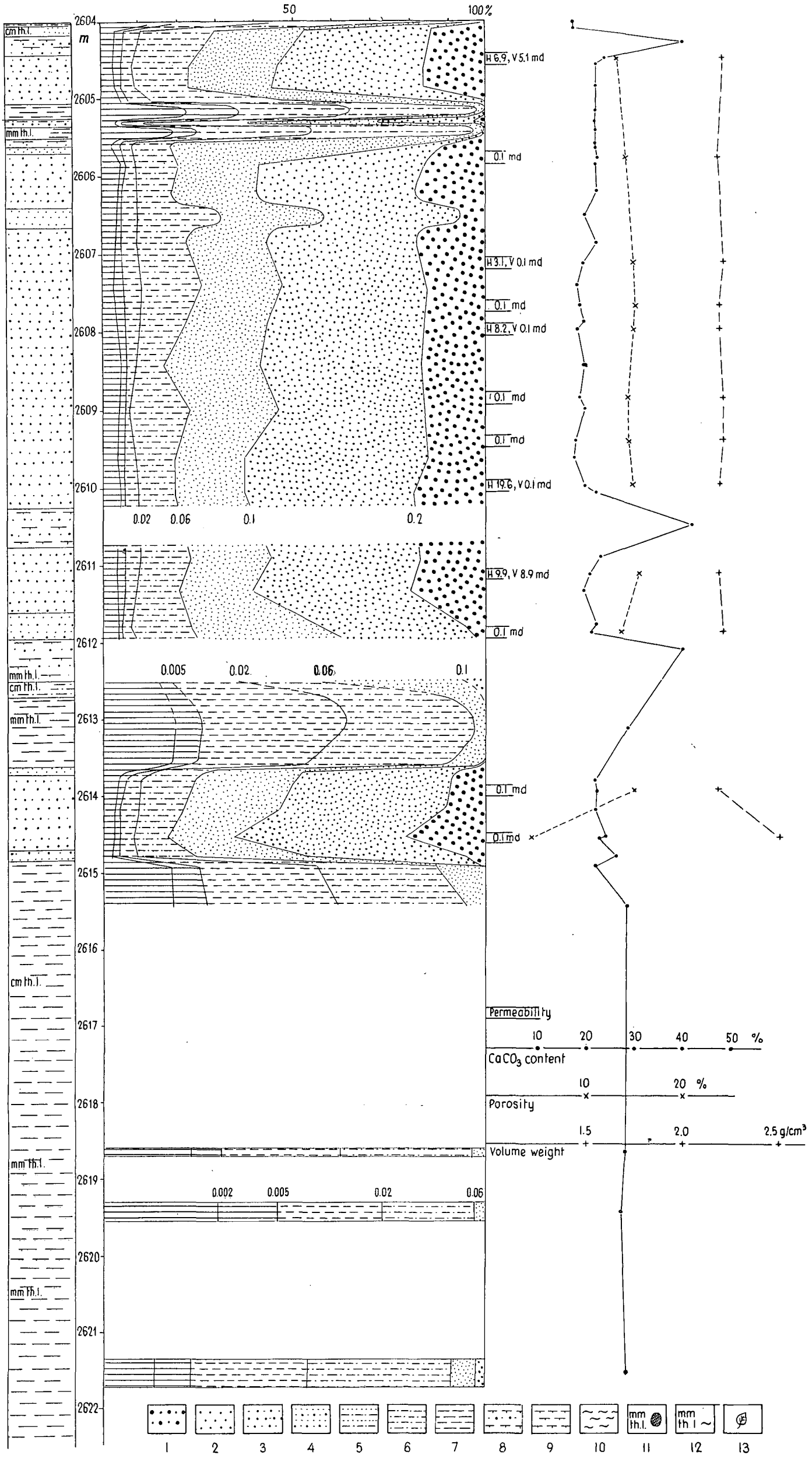


Fig. 4. Granulometric and petrophysical data of the core of borehole Algyő-248. *Lower Pannonian.* *1.* Fine-grained sandstone with medium-grained sand, *2.* Fine-grained sandstone, *3.* Very fine sandy fine-grained sandstone, *4.* Fine sandy very fine-grained sandstone, *5.* Aleurolitic fine-grained sandstone, *6.* Very fine sandy coarse-grained aleurolite, *7.* Coarse aleurolitic very fine-grained aleurolite, *8.* Calcareous sandstone, *9.* Clay-marl, *10.* Marl. Lime-marl, *11.* Finely laminated sediment with micaceous laminae of mm order in thickness, *12.* Finely laminated sediment with coalified vegetal detritus forming laminae of mm order in thickness, *13.* Coalified vegetal detritus

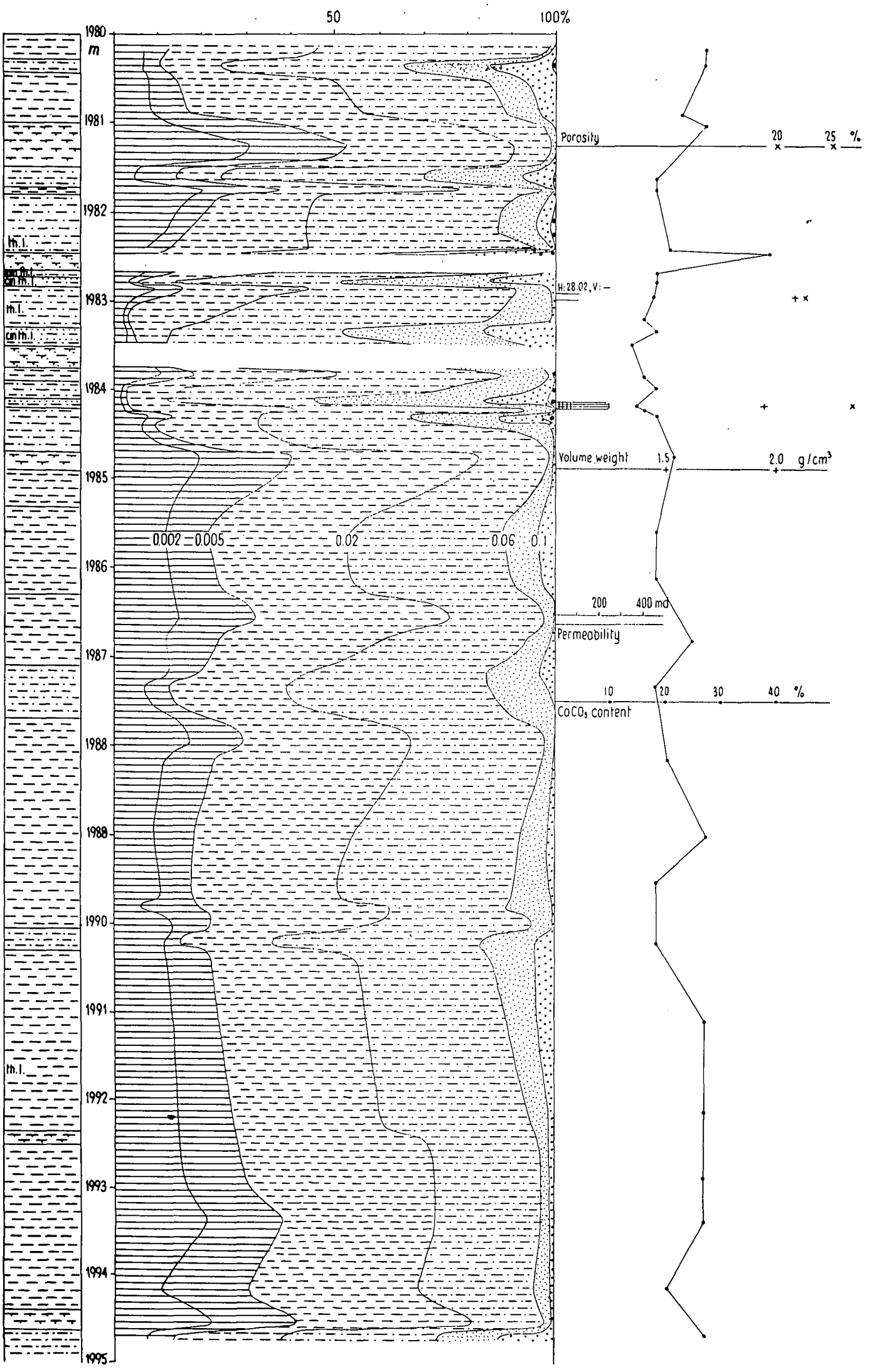


Fig. 5. Granulometric and petrophysical data of the core of borehole Algyő-254. *Upper Pannonian.* Legend, see Fig. 4.

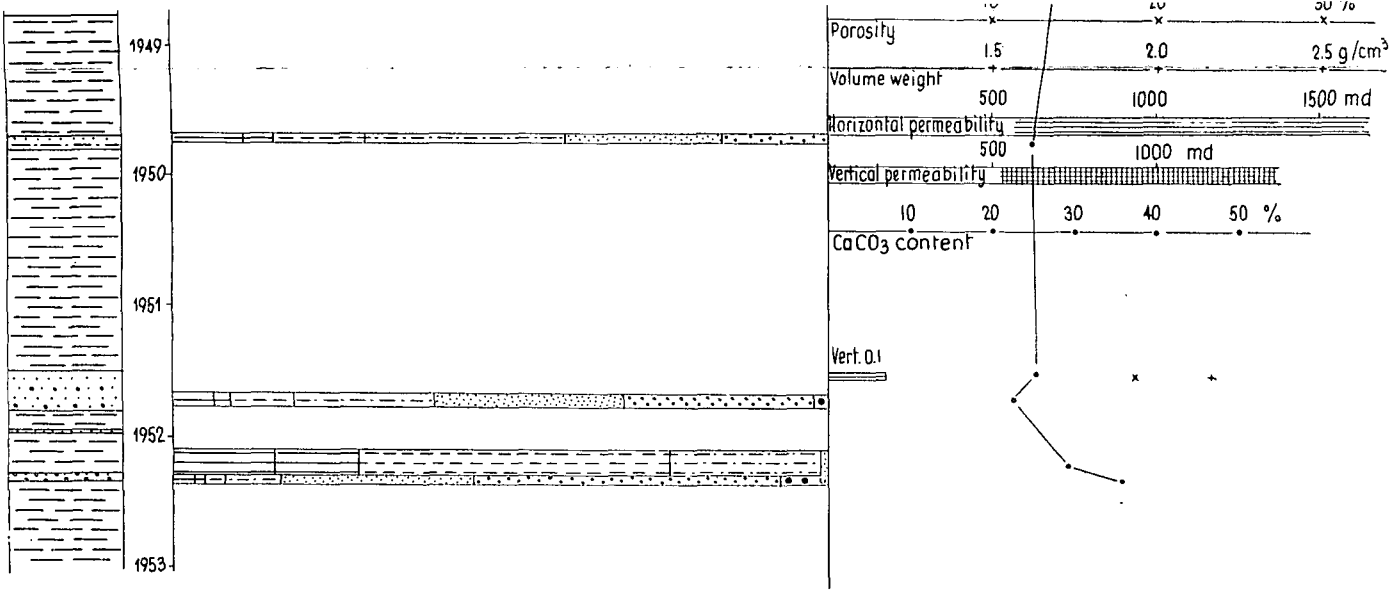
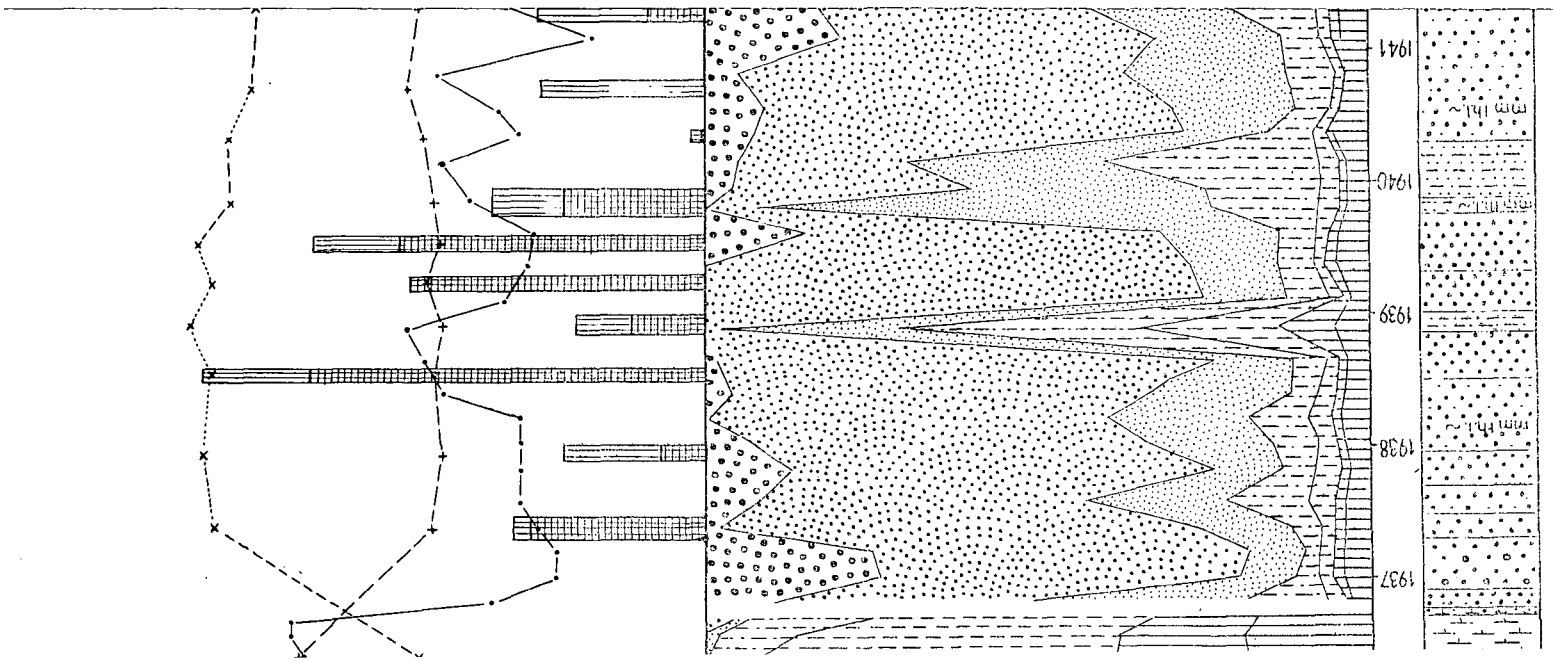


Fig. 6. Granulometric and petrophysical data of the core of borehole Algyő-198. *Upper Pannonian.*
Legend, see Fig. 4.



mm th.
cm th.
1939
1940
1941
1942
1943
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1945
1946
1947
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0.005
0.02
0.06
0.01
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0.02
0.1 md
0.1 md
0.1 md
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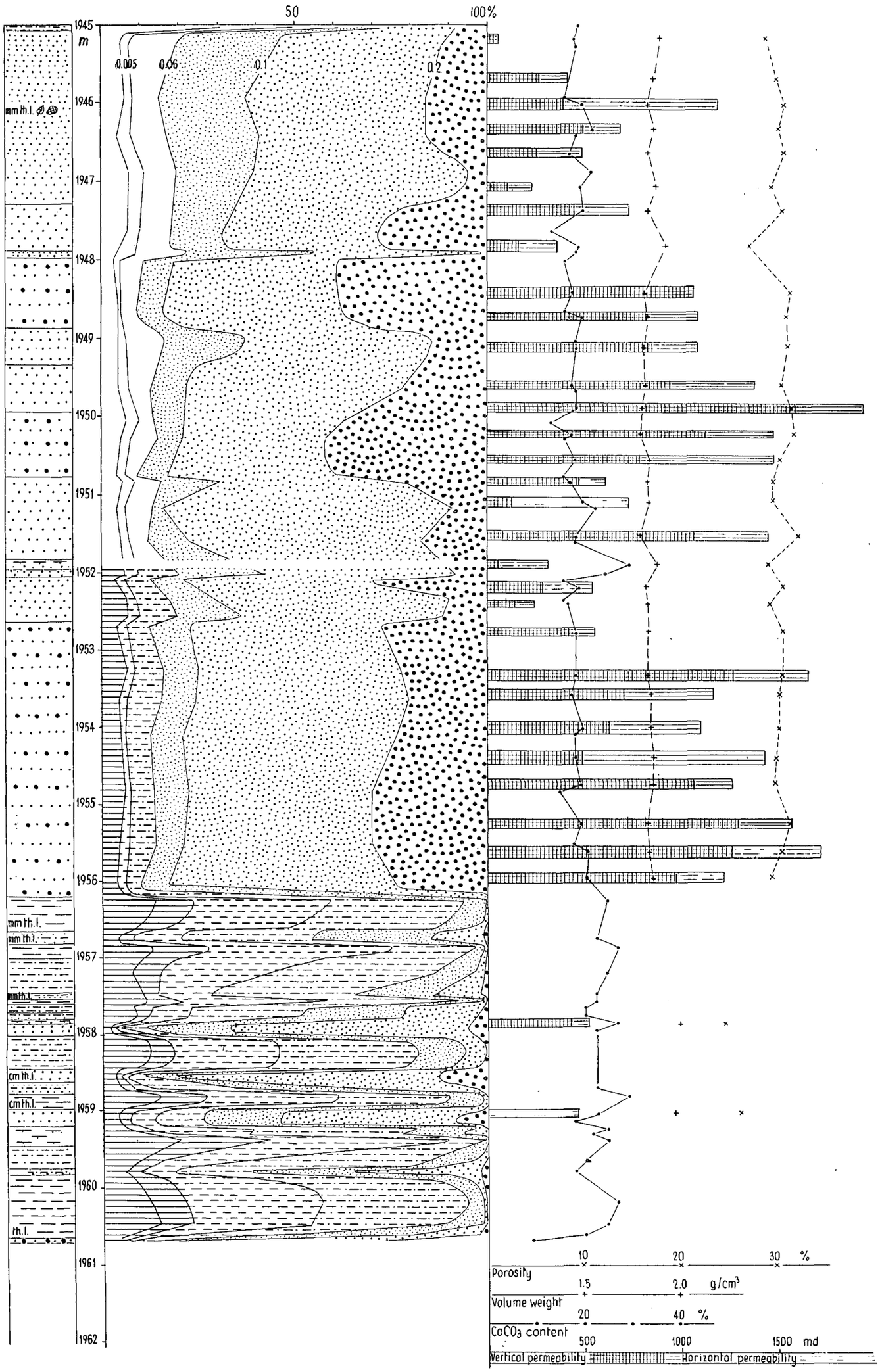


Fig. 8. Granulometric and petrophysical data of the core of borehole Algyő-242. *Upper Pannonian.*
Legend, see Fig. 4.

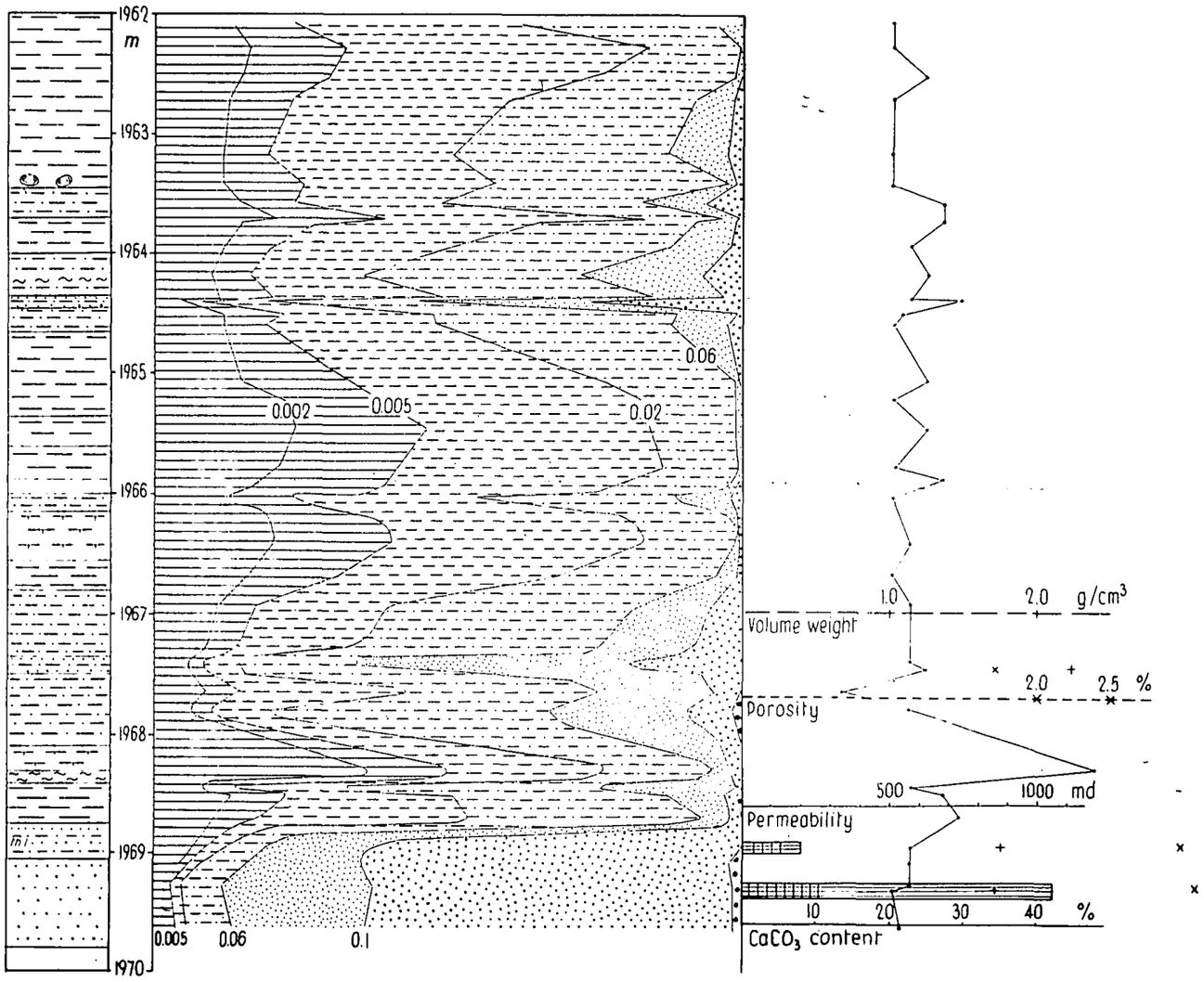


Fig. 9. Granulometric and petrophysical data of the core of borehole Algyő-242. *Upper Pannonian.*
Legend, see Fig. 4.

younger phases of the Lower Pannonian and this is proved also by the deposition of the strata assigned to this period. The presence of the shallower type is further evidenced by the frequency of the double-sheet structure built up by coalified plant detritus and other rocks. Locally, the bores traversed also coal sheet of centimetres thickness. Regarding their origin these are allochtonous. The shallowing of water, the greater frequency of the rhythms built up by A B C D / A... types in the upper part, as well as the change of the sedimentary features indicate the filling up of the basin, i.e. the advance of shore line.

Taking the whole of the investigated area the thickness of the Upper Pannonian sediments changes between 500 and 1700 metres. The thinner formations, similarly to those mentioned above, are found above the basement of relatively uplifted structural position. The sediments are also of rhythmic structure. These are separated from the Lower Pannonian sediments by hardly observable angular unconformity. The angular unconformity was caused by the change of facies.

The sediments of this period are varied: in addition to the predominant types, *i.e.* fine sandstone, very fine sandstone, coarse aleurolite, fine aleurolite, less clay-marl, other types, *e.g.* gravelly sandstone, medium-grained sandstone, marl, lime-marl, woody brown-coal, coaly clay and humic rocks also occur.

Based on about 3 000 data the value of the part dissolving in cold hydrochloric acid proved to be 23 per cent, the extreme values were 0 and 85 per cent. As compared to the values of the Lower Pannonian the bulk density decreased (1.7 to 1.9 g/cm^3), the values of porosity and permeability increased and this is demonstrated in *Figs. 5—10.* It is to be noted that in case of the less compacted samples found next the surface (which are neglected in this study) the investigation results changed in accordance with the data of literature.

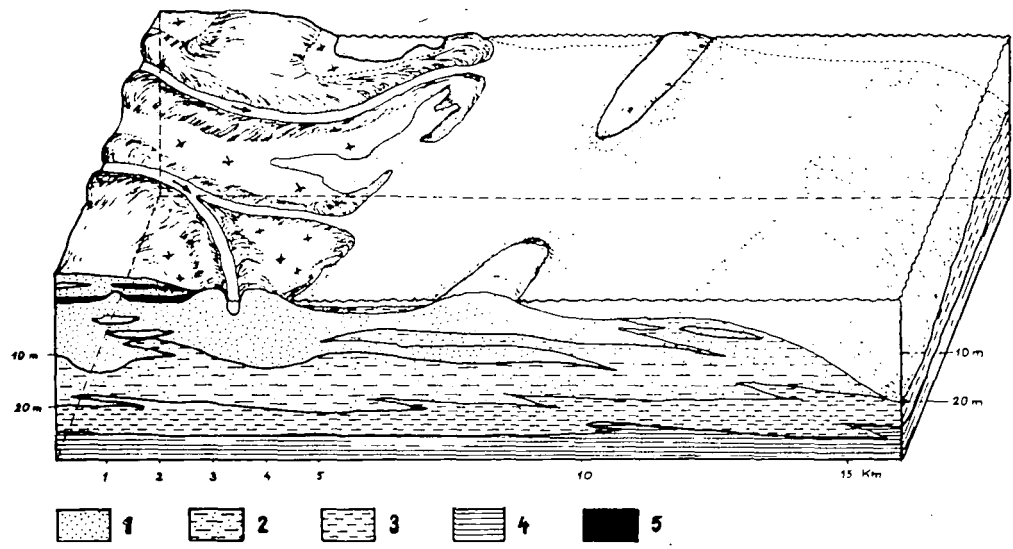


Fig. 10. Schematic block diagram illustrating the sedimentary environments at the beginning of the Upper Pannonian.

1. Sandstone, *2.* Sandstone and aleurolite, *3.* Aleurolite, *4.* Clay-marl, *5.* Coal

The statistic parametres computed from the great number of grain size distribution of the sandstones and of certain areas, evidenced that in the course of accumulation the energy states have considerably changed both in space beside each other and in time above one another.

Several researchers dealt with the classification of the Upper Pannonian sequence but there are considerable differences between the statements [BARTHA, F., 1971 and 1974; JÁMBOR, Á., KORPÁS, L., HÓDI, M., 1971; JASKÓ, S. 1974; KŐRÖSSY, L. 1968—1973, and STRAUSZ, L. 1971]. As to our opinion the divergences of views are based upon the fact that in case of the classifications based either on paleontology or on lithofacies they simplified the mechanism of filling up of the Carpathian Basin and of its part-basins and drew generalizing conclusions from the thin strata sequences of the surficial outcrops.

Our investigations detailed have discovered phenomena which cannot be build-in into the previous imaginations. First of all the Algyő-Szeged area explored in details by bores (about 500 bores) made possible to draw the conclusions. *E.g.* the core samples contained occasionally one or two rounded quartz pebbles and gravel band imbedded in sandstone and aleurolite groundmass, further they contained lime concretions which from here upward show a systematic appearance! The intercalations of autochtonous coaly-clay — woody brown coal — coaly clay of max. 1 m thickness are frequent. Their arrangement within one rhythm shows areally and vertically regular development. The coalified plant remnants of vertical position occur also in connection with the area and with horizon within the rhythm. Imprints of leaves of deciduous trees of good preservation and from the middle part of the Lower Pannonian Equisetum remnants are frequent. In about the lower third of the Upper Pannonian sequence the grain size composition becomes tendentiously coarser upward within one rhythm so, that in the few metres closing the rhythm it suddenly transforms into the clay-marl separating the single rhythms. In the areas containing woody brown coal bands the strata of this re-transformation is marked by coal bands. The areal changes of grain size composition of the rhythms are also tendentiously directed (refinement to NW-SE). In the rhythms overlying each other the areas of coarser grain size composition and the coaly intercalations are displaced also to the SE. On the basis of the sandstone thicknesses accumulations of "channel-filling" could be fixed within one rhythms.

Similarly to the Lower Pannonian the boundaries of rhythms were delineated in clay-marls. From these *Limnocardium, Congeria* and *Valenciennesia* fauna was found which were poor in species. Only one species, the *Limnocardium* (Paradacna) *abichi* R. H. var. appears in predominance, on the other side bound to coaly strata the fresh-water forms, e.g. *Psilunio, Unio, Viviparus, Planorbis,* etc. appear in small number. Fauna was found only sporadically in other rhythm members. Palynological investigations relate to the neighbourhood of gallery forest along watercourses and morass environments.

The stratification types and the other sedimentary features are in accordance, resp., can be explained with the features listed above.

These data evidence the presence of delta sedimentation and its environments in the lower third of the Upper Pannonian investigated in details.

From other research areas of the South Great Plain similar sediments were collected relating to the common extension of the fluvio-lacustrine environments. The apparent contradiction, i.e. "everywhere delta at the same time" at the beginning of the Upper Pannonian was resulted in by the fact that the separation from the Lower Pannonian was based on the change of lithofacies and this was considered

the time-boundary. As to our opinion, the Great Hungarian Plain is considered a uniform geosyncline and the filling up of the basin from the margins started already in major part of the Lower Pannonian, i.e. the formation of the Upper Pannonian environments has begun. In addition to the features of delta accumulations, the periodic epirogenic subsidence of the basin is responsible for the rhythms overlying each other. In addition to these two most important factors other reasons can also be mentioned, *e.g.* the extension of the erosion area, the working capacity of rivers, the system of redepositing-levelling factors within the geosyncline, etc. According to our hypothesis this transgressing "Upper Pannonian" environment replaced the Lower Pannonian inland lake in the whole of the area within a greater time interval, consequently no isochronism can be attributed to the petrological and paleontological (molluscs) delineation, either. To fix recently the time horizon can be carried out only relatively by smaller units. In our case, in the South Great Plain, *e.g.* in Algyő the sandy sequence put into the lower part of the Upper Pannonian is contemporaneous with the completing sediments assigned to the Lower Pannonian and lying southeast and east of it. Taking into account the megaunits, the buried block-range of Battonya with its related deep-zones was filled-up from the Bihar Mountains which follows from its structural and geographical location.

In the following periods of the Upper Pannonian the spatially neighbouring Upper Pannonian sediments accumulated in a shallow fresh-water lake-systems and in their close neighbourhood from the rivers filling up the lakes themselves. Temporally, above one another a similar system can be observed. In a given smaller part-unit and in definite time the predominating regime is determined by the relation of the measure of filling-up and of the epirogenic subsidence (compaction), since block-like irregular subsidence is evidenced by the differences of thicknesses.

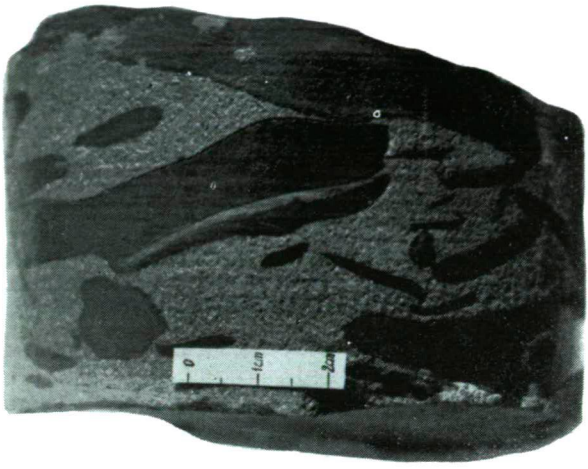
From the medium third part of the sequence the change is apparent, *i.e.* the the sediments hardly diagenized, the clay-marl disappear. In this phase the aleurolite with plant remnants and concretions predominates. The upper third is of sand formation again and the coaly intercalations are more frequent, as well.

From the Upper Pliocene up to the Holocene the sedimentary environments mentioned above are replaced tendentiously by the predominance of the terrestrial facies.

In the course of making this study authors used the results of several geologists of the OKGT, i.e. of ÁKOS LELKES, LÁSZLÓ MAGYAR and JÁNOS TANÁCS. Special acknowledgement is given for the valuable advices of DR. JÓZSEF MEZŐSI.

SUMMARY AND CONCLUSIONS

On the basis of the core sample processing of several years, authors state that the detailed sedimentological investigation of the rock material of core samples is a successful possibility to know the Neogene sequence. The studying of the horizontal and vertical connections of the paleogeographic "snapshots" obtained in this way in details makes possible the research of the temporal and spatial changes of geological evolution of an area explored by numerous bores, and taking always into consideration the limited possibilities of geological cognition.



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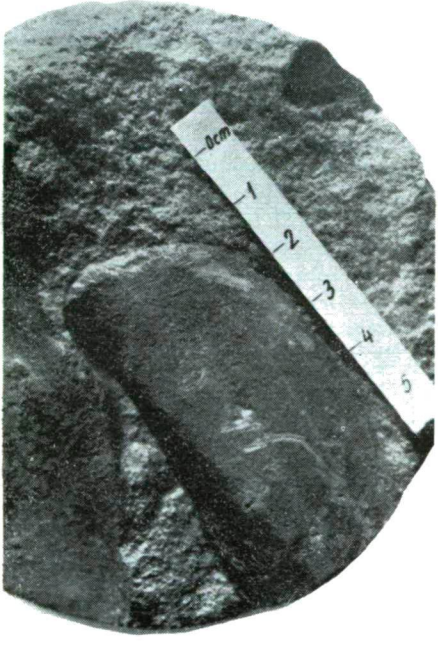

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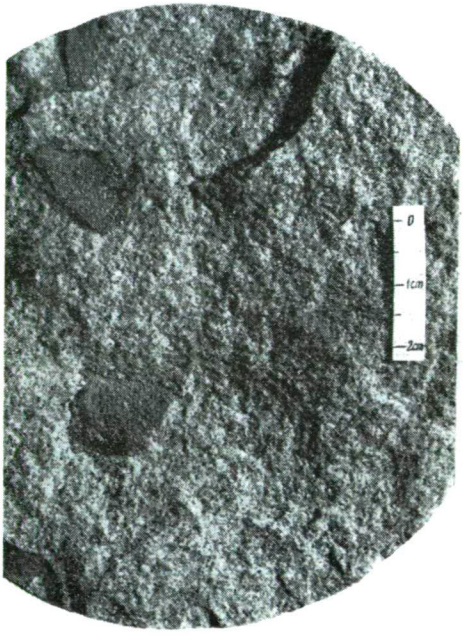

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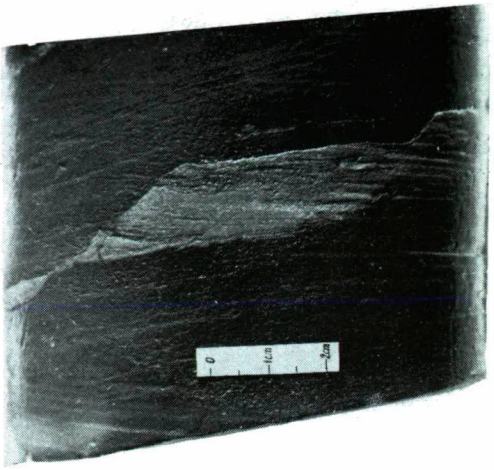

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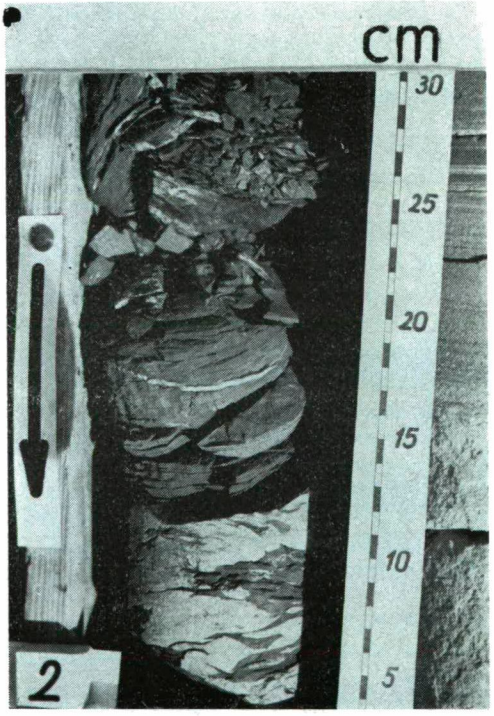

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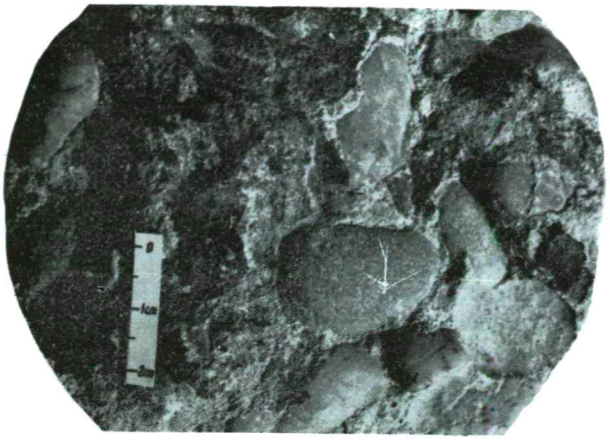

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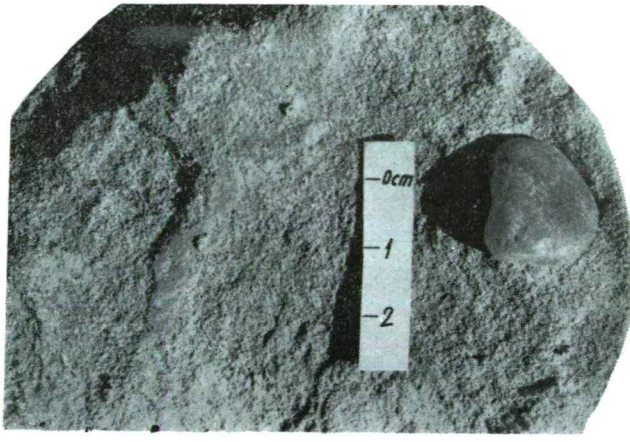

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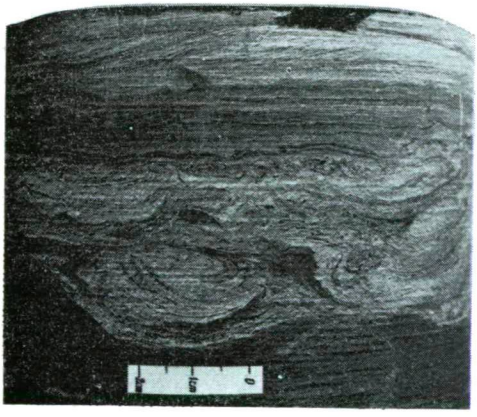

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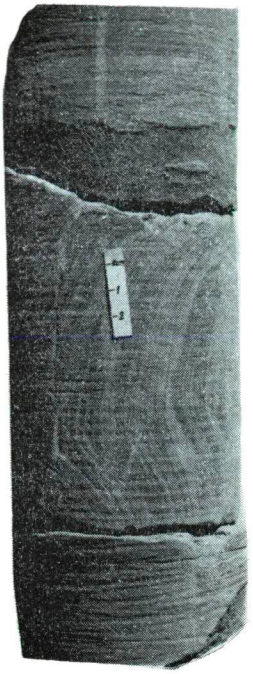

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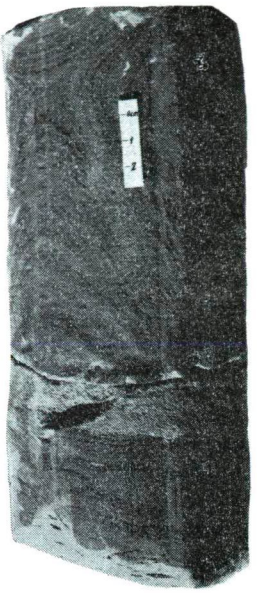

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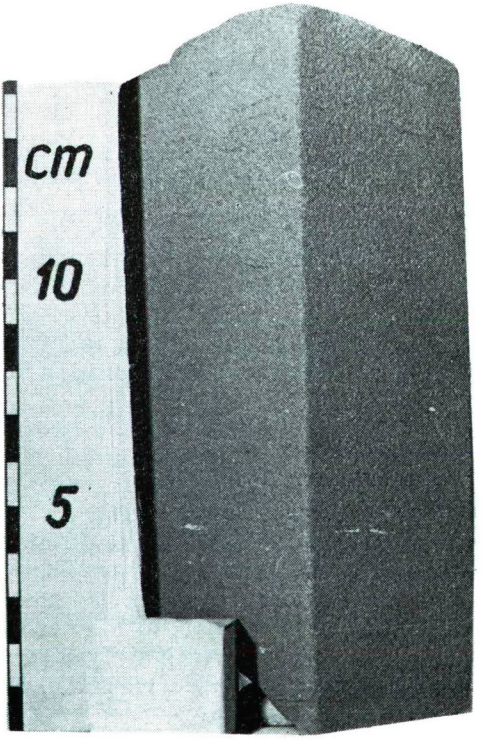

3

EXPLANATION OF PLATES

PLATE I

1 and 2 Sandstone containing clay-marl pebbles. Lower Pannonian. — Borehole Algyő-248 2600,62—2601,05 m

3 Sandstone with plant debris and fine-grained aleurolite pebbles. Lower Pannonian — Borehole Algyő-92 2468,40 m

PLATE II

1 Fine-grained aleurolite holding very fine-grained sandstone lens. Micro-fault was formed by the effect of compaction. Lower Pannonian. — Borehole Algyő-86 2421 m

2 Sandstone and aleurolite having folded bedding. Lower Pannonian. — Borehole Algyő-264 2414,05—2414,23 m

3 "Rolling" clay-marl and fine-grained sandstone. Lower Pannonian. — Borehole Ferencszállás-13 2385—2395 m

PLATE III

1 Gravel band with coaly plant debris in sandstone. Upper Pannonian. — Borehole Algyő-19 2107-60 m

2 In sandstone there is a rounded quartz pebble. Upper Pannonian. — Borehole Algyő-230 1956,4 m

3 Convolution of sand waves sunken by differential load into the under lying siltstone. Upper Pannonian. — Borehole Algyő-242 1965,4 m

PLATE IV

1 and 2 Sandstone characterized by grain size change having horizontal and chaotic laminated parts with erosive surface aleurolit pebble. Upper Pannonian. — Borehole Algyő-241 2017,30—2017,58 m

3 Fine-grained sandstone without interbedding. Upper Pannonian. — Borehole Algyő-194 1937,0—1937,5 m

The most important conclusions are as follows:

1. In the investigated area the last sedimentary cycle (From the Helvetian up to the Holocene) is uniform and free of intermediary greater regressions; its accumulation had been continuous at a given place.

2. In the Carpathian Basin the "climax" of the marine facies can be put at the Tortonian though the local increase of inundation may occur in addition of the slow regression of the whole basin.

3. The oldest formation of the Neogene is for the most part of clastic formation, in single parts of areas or in single bores its age may be Helvetian, Tortonian, Sarmatian and Lower Pannonian; but when accumulation has started the cycle had been continuous up to the Recent.

4. Since the Upper Miocene the brackish environment is replaced gradually by fresh-water environments and the individual evolution of the geosyncline being independent of the Pontian-Caspian Basin strated.

5. During the Miocene and Lower Pannonian there are considerable differences within the geosyncline (depth of water, salinity, bottom-relief, transportation and movement directions of the sediments, rock facies) and the environment is euxinic.

6. In the Upper Pannonian a fluvio-lacustrine system has developed which had been ceased by the human intervention in the Holocene.

7. The limitation of the Lower and Upper Pannonian by the quantitative increase and fauna content of the sand sediments is conventional and this does not mean a uniform time-demarcation of the whole of the area.

8. The sandstones assigned to the Lower Pannonian are coat-sands accumulated under uniform inundation of water while those of the Upper Pannonian are connected to delta sedimentation and shallow-water environments.

9. Upward from the boundary of the Lower and Upper Pannonian autochtonous coal-bed bearing sections are found in several horizons being of thin, *i.e.* of several cm (up to 1 m) thickness; these are the regular occurrences of the morassic environments.

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CLAY MINERALS OF THE SOUTHERN GREAT HUNGARIAN PLAIN

I. VARSÁNYI

INTRODUCTION

Core samples from two boreholes of "Makó—Hódmezővásárhely trench" were studied. This area extends on the southern part of the Great Hungarian Plain. Samples of Makó-1 and Makó-2 drillings represent the sedimentary sequences of the internal part of this Neogene basin having a relatively deep structural position [MUCSI, 1973].

The results of present paper give informations on the clay mineral content of formations of the Upper and Lower Pannonian substages and that of the Miocene epoch.

The Upper and Lower Pannonian according to the Hungarian classification correspond about to the Lower and Middle Pliocene, but the border between the Upper and Lower Pannonian does not coincide with that of the Middle and Lower Pliocene. The ages of the Miocene samples are Middle and Upper Miocene.

The border of the Upper and Lower Pannonian is at the depth of about 2300 m in the area investigated. The border between the Lower Pannonian and Miocene may be at 4156—4162 m.

The Makó-1 drilling ends in the Lower Pannonian substage, the Makó-2 went through the Neogene sequences and reached the bottom of the basin.

METHODS

After having been removed the amounts of carbonates and organic matter mica, montmorillonite, chlorite, kaolinite, quartz, feldspar and amorphous material were determined by chemical methods in the fraction of 10 μ of core samples.

ALEXIADES and JACKSON [1965] summarize the method as follows. The mica content was based on 8,29 % K (10 % K_2O) of mica. Quartz and feldspars were determined by the pyrosulfate fusion method [KIELY and JACKSON, 1964]. The amorphous material was based on the SiO_2 plus Al_2O_3 dissolved by 0,5 N NaOH treatment, with 10 % H_2O added, while kaolinite plus halloysite was based on the difference in Si and Al dissolved by 2,5 min of boiling in 0,5 *N* NaOH from samples heated for 4 hours at 525 °C and 110 °C [ALEXIADES and JACKSON, 1966]. Chlorite was determined [ALEXIADES and JACKSON, 1966] by measuring the total water of K-saturated samples by ignition loss between 300 to 950 °C, after a deduction of % water loss (300 °C basis) attributable to the other clay minerals present. The vermiculite and montmorillonite contents were derived from cation-exchange capacity (CEC) determinations.

EXPERIMENTS AND CONCLUSIONS

The mineralogical composition of 10 μ fraction of the samples is indicated in Table 1 and Table 2.

The chlorite and amorphous material contents of the samples Makó-1 and Makó-2 are different.

TABLE 1

Minerals present in the core samples from Makó-1 borehole

	Na-feldspar	K-feldspar	Quartz	Amorphous material	Kaolinite	Montmorillonite	Chlorite	Mica	Total
I.	2,3	1,0	19,6	7,7	4,6	24,1	11,7	22,1	96,1
II.	3,6	0,8	18,0	7,3	0,0	15,8	18,3	26,9	88,7
III.	2,1	0,5	10,1	9,6	4,9	21,1	12,7	27,3	88,3
IV.	3,6	1,5	22,0	5,2	5,4	20,7	11,8	25,5	95,8
V.	1,9	0,9	20,6	5,9	3,5	12,5	18,4	24,5	88,2
VI.	1,9	1,1	21,0	3,7	3.3	13,8	18,8	24,3	87,9
VII.	4,9	1,2	19,6	9,8	1,7	0,0	22,8	25,6	85,6
VIII.	5,3	2,2	13,8	4,5	2,9	14,2	20,1	28,6	91,6
IX.	3,1	1,8	16,8	2,7	0,9	15,2	20,7	26,2	87,4
X.	4,0	1,3	20,2	2,6	0,0	16,3	27,8	25,3	97,5
XI.	3,9	1,1	11,5	4,7	0,0	8,1	29,9	27,6	86,5
XII.	4,4	0,6	17,4	4,6	1,9	5,8	21,6	26,9	82,2
XIII.	3,2	0,8	19,6	16,2	0,0	1,0	25,4	26,4	82,4
XIV.	3,8	0,4	19,4	9,1	0,0	8,9	18,7	28,8	89,1
XV.	2,3	0,2	13,5	0,6	0,0	19,0	22,0	26,2	83,3
XVI.	6,8	1,3	23,0	1,2	0,3	10,2	24,4	28,2	95,4
XVII.	3,7	0,4	16,9	0,5	0,0	11,1	24,4	31,6	88,6

This difference may be in connection with the time of acid pretreatment carried out to remove carbonates. The time of this pretreatment was longer at the Makó-1 than Makó-2 samples, so one part of chlorite could dissolve, and the amount of amorphous material increased.

The chlorite and mica contents are predominant in the samples of both borings, however, several samples contain considerable amount of montmorillonite. The chemical method used does not give any information whether the montmorillonite is present as a discrete phase or as a component of a mixed-layer structure. According to the previous *X*-ray investigations the montmorillonite occurs in illite-montmorillonite mixed-layer minerals in these samples [MEZŐSI, 1974]. However, the occurrence of the mixed-layer illite-montmorillonite minerals could be indicated by *X*-ray diffractometry only in few samples and the quantity determined is also less than by chemical method.

The kaolinite content is small and it disappears at the border of the Upper Pannonian and Lower Pannonian in the Makó-1 drilling but in the Makó-2 drilling kaolinite is present in each determined sample.

The quantity of quartz is similar in both drillings and amounts to about 20%.

Na-feldspar is in larger quantity than K-feldspar but even Na-feldspar is under 10% except in the Miocene psammites and rudites where its quantity is over 10%.

TABLE 2

Minerals present in the core samples from Makó-2 borehole

	Na-feldspar	K-feldspar	Quartz	Amorphous-material	Kaolinite	Montmo-rillonite	Chlorite	Mica	Total
1	3,2	0,7	15,7	3,7	4,6	16.4	33,4	26,0	103,7
2	3,7	0,6	14,9	2,6	4,4	21,5	30.4	28,9	107.0
3	7,6	1,4	13,5	3,6	3,8	17,1	18,1	31,7	96,8
4	5,3	0,4	13.4	2.3	3,6	17,3	25,1	34.6	102,0
5	10,0	4,2	20,1	2,0	0,0	25,6	25,6	20,4	107,9
6	4,9	1,1	17.3	3,0	0,6	8,0	35,4	35,6	105,9
7	7,5	1,4	17,9	3,8	0,7	3,1	34,6	34,6	103,6
8	7,8	2,5	19,6	2,8	0,5	6,1	32,1	32,2	103,6
9	7,6	2,4	15,4	4,9	1,4	16,6	20,2	27,3	95,8
10	6,9	2,1	18,9	1,3	0,9	1,5	38,5	26,8	96,9
11	3,7	2,1	22,5	1,5	3,0	10,5	34,9	27,7	105,9
12	4,2	2,0	21,9	1,4	3,0	10,7	39,0	27,6	109,8
13	4,2	0,9	23,4	1,2	3,0	6,6	42,1	28,5	109,9
14	4,8	1,0	20,1	1,0	2,5	10 4	40,5	28,9	109,1
15	4 8	3 2	23,6	2,7	2 0	12,5	38,5	22,6	109,9
16	2,3	0,5	16,8	1,7	3,2	12,4	45,0	27,4	109,3
17	5 4	2 5	19,9	2,5	2,4	5,4	38,8	25,5	102,4
19	3,4	0,5	18,7	2,8	1,0	8,0	50,8	29,3	109,7
20	4,1	0,2	19,8	2,0	3,1	13,6	33,6	28,3	104,7
21	5,1	0,4	22,1	1,6	0,7	5,0	45,5	28,9	109,3
22	3.9	0,0	18,8	2,2	2,3	11,2	38,2	31,6	108,2
24	2,7	0,0	20,1	2,4	2,7	8,1	32,2	33,3	101,5
25	1,3	0,1	32,8	2,5	1,1	16,4	18,9	36,7	109,8
26	19,6	0,0	12,9	1,9	1,6	22,0	16,5	35,0	109,5
27	12,3	0,4	7,5	2,3	0,7	12,3	41,7	32,1	109,3
28	13,1	0,8	23,6	3,1	0,4	11,6	18,0	25,5	95,1
29	11,6	0,0	28,6	1,6	2,2	12,0	23,2	25,1	104.3
30	12,9	0,6	30,4	2,0	1,2	10,1	19,2	24,4	100,8
31	9,7	0,2	12,8	2,0	1,4	3,1	24,5	35,6	89,3
32	11,0	0,0	15,1	1,9	1,1	2,4	26,1	39,3	95,9

The average values of mineral contents were calculated and listed in Table 3 for the Upper and Lower Pannonian and Miocene samples.

As it can be seen the means in the two drillings are very similar. Means of kaolinite, montmorillonite and amorphous material change in the same way, they are the same in the Lower Pannonian and Miocene samples and they increase in the Upper Pannonian.

The Miocene and Lower Pannonian average values of chlorite are also the same and the chlorite content of Upper Pannonian samples is less.

The mica and Na-feldspar contents increase in order of Upper Pannonian, Lower Pannonian and Miocene. The quantity of quartz changes similarly but the increase is small.

Considering, however, the Miocene pelites and Miocene psammites and rudites, respectively, this sequences may be modified.

Besides the average values the study of the distribution of the minerals with the depth is important because it gives more information on the types of changes than the study only of the means.

The changes of the amounts of the minerals in function of the depth are shown in Fig. *1*.

Changes in contents of minerals with the depth are different in the Miocene pelites and Miocene rudites and psammites, similarly to that of the means.

In rudites and psammites the values fluctuate strongly and the tendency of changes differs from changes in the pelitic sediments.

In the Upper and Lower Pannonian samples kaolinite and montmorillonite contents decrease with the depth of burial, chlorite increases and mica increases, too, but less than chlorite. In the Miocene pelites the quantities of montmorillonite and kaolinite are constant, mica increases but chlorite decreases.

The distribution of clay mineral contents is influenced by a great number of factors. Among these the most important ones are the source material, the environment of sedimentation, the distance from the shore and changes during sedimentation and after burial.

TABLE 3

Means of the minerals present in the Upper Pannonian, Lower Pannonian and Miocene samples

		Na-feldspar	K-feldspar	Quartz
Makó-1	Upper Pannonian	3,2 (9)	1,2	17,9
	Lower Pannonian	4,0 (8)	7,0	17,7
Makó-2	Upper Pannonian	3,4 (2)	0,6	15,3
	Lower Pannonian	5,8 (14)	1,8	18,9
	Miocene (total)	8,3 (14)	0,4	20,2
	Miocene pelites	4,1 (6)	0,6	19,9
	Miocene rudites	11,4 (8)	0,3	20,4
Means of the	Upper Pannonian	3,2 (11)	1,1	17,4
two borings	Lower Pannonian	5,1 (22)	1,4	18,4
	Miocene (total)	8,3 (14)	0,4	20,2
	Miocene pelites	4,1 (6)	0,6	19,9
	Miocene rudites	11,4 (8)	0,3	20,4

The number of the samples are in bracket.

Amorphous material	Kaolinite	Montmorillonite	Chlorite	Mica
6,2	3,0	15,2	17,2	25,7
3,3	0,3	10,0	24,3	27,6
3,1	4,5	18,9	31,9	27,5
2,4	2,0	10,6	33,5	29,0
2,2	1,6	10,1	30,4	30,7
2,2	2,0	8,5	39,8	29,5
2,1	1,2	11,2	23,5	31,8
5,6	3,0	15,9	19,9	26,0
2,7	1,4	10,4	30,2	28,0
2,2	1,6	10,1	30,4	30,7
2,2	2,0	8,5	39,8	29,5
2,1	1,2	11,2	23,5	31,8

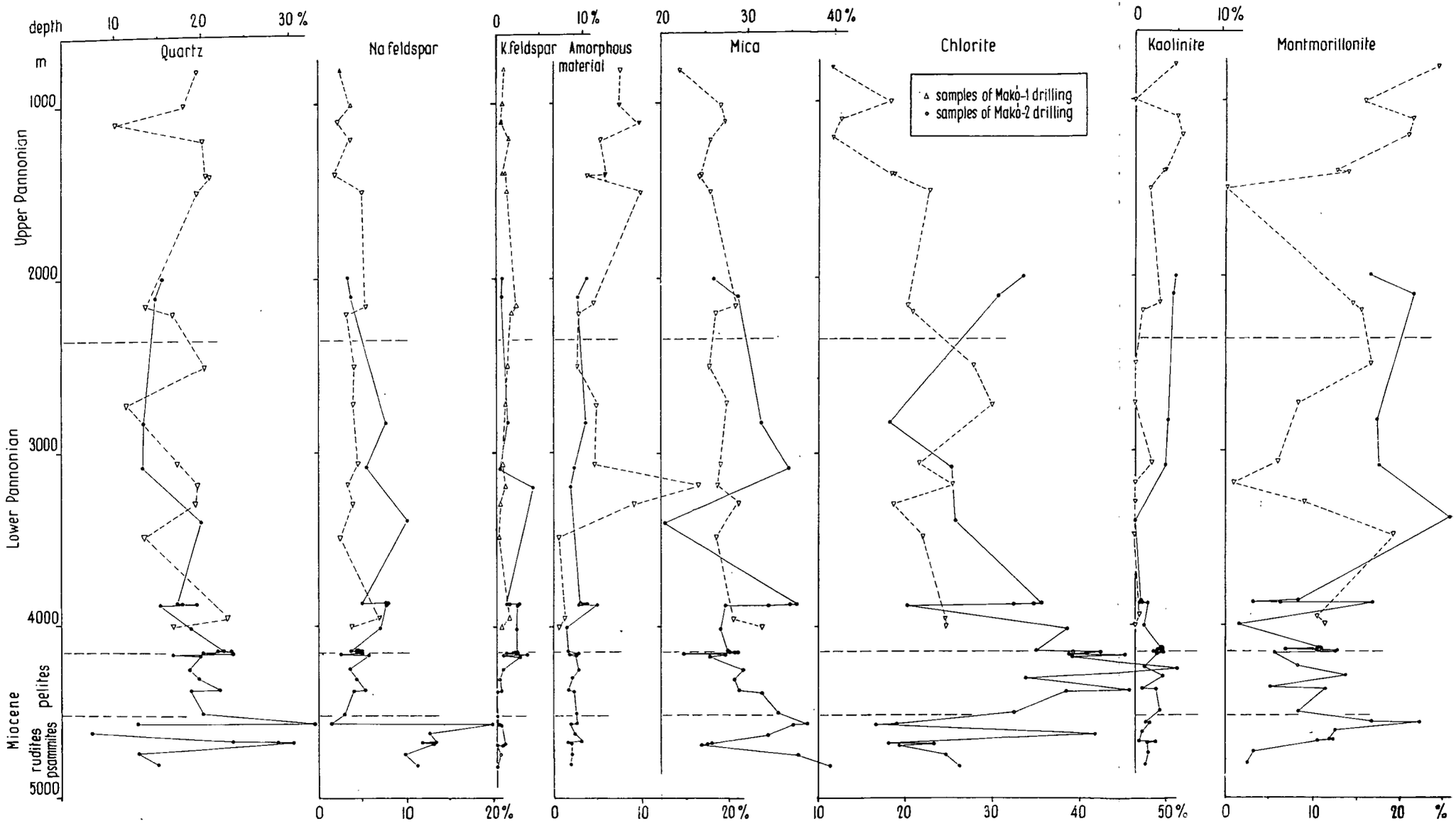

Fig. 1. The amount of minerals in function of the depth

The effect of the individual factors can't be separated, nearly their joint effect can be observed by studying the clay mineral distribution.

The increase of chlorite and mica, the decrease of montmorillonite and kaolinite contents are well known diagenetic changes after burial [GRIM, 1953].

Similar changes in the clay mineral content of the samples investigated suggest diagenetic alterations in this area, too. Decrease in amorphous material with the depth shows the increase of crystallinity which also took place during diagenesis [MURRAY and SAYYAB, 1955].

The distribution of clay mineral content is influenced not only by the diagenesis but by other factors, too. Appearance of the kaolinite in the Miocene may be in connection with the distance from the shore. During sedimentation in the Miocene this part of the "Makó—Hódmezővásárhely trench" had a nearshore position and because of differential flocculation originally more kaolinite could be present [WHITEHOUSE and MCCARTER, 1958] than in the Lower Pannonian when due to the sinking

TABLE 4

Oxidation ratios and $\frac{mica+chlorite}{montmorillonite+kaolinite}$ *(k) values of the samples from Makó-2 boring*

Samples	Depth	Oxidation ratio		*k*
		original	fraction of 10μ	
1	1990,00—1992,40	0,138	0,629	2,82
2	2102,00—2104,60	0,161	0,534	2,29
3	2825,10—2825,20	0,044	0,433	2,38
4	3086,64—3087,80	0,092	0,404	2,85
5	3395,46—3395,58	0,151	*	1,80
6	3870,00—3870,27	0,169	0,423	8,25
7	3872,71—3872,84	0,107	0,339	18,20
8	3873,83—3874,02	0,074	0,433	9,74
9	3875,45—3875,57	0,000	0,312	2,64
10	4014,70—4014,80	0,074	0,495	27,20
11	4140,13—4140,24	0,108	0,275	4,64
12	4145,07—4145,36	0,140	0,244	4,86
13	4145,70—4145,78	0,140	0,259	7,35
14	4146,40—4146,50	0,106	0,294	5,38
15	4152,20—4152,30	0,148	0,280	4,21
16	4156,20—4156,30	0,097	0,313	4,64
17	4162,64—4162,80	0,172	0,518	8,24
18	4176,22—4176,32	0,162	0,336	*
19	4245,25—4245,39	0,178	0,467	8,90
20	4310,70—4301,97	0,127	0,286	3,71
21	4371,02—4371,29	0,121	0,260	13,05
22	4379,45—4379,65	0,116	0,388	5,17
23	4501,48—4501,72	0,045	0,430	*
24	4509,25—4509,65	0,075	0,345	6,06
25	4565,70—4565,84	0,182	0,465	3,18
26	4567,60—4567,71	*	*	2,18
27	4620,35—4620,47	0,289	0,593	5,68
28	4672,30—4673,10	*	0,408	3,65
29	4673,10—4674,60	0,246	*	3,40
30	4674,60—4675,60	*	*	3,86
31	4735,10—4735,22	0,280	0,396	13,35
32	4800,50—4803,60	0,445	0,180	18,68

* There were not enough quantities of samples to carry out these analyses.

of the basin and its filling up with water the place investigated got into the centre of the basin so the quantity of kaolinite decreased.

In Miocene samples quantity of chlorite does not increase with the depth. These samples are more oxidized than it may be expected on the basis of the depth, and therefore diagenetic alterations can be restricted by the environment. The oxidation ratio $\left[\frac{2\,Fe_2O_3}{2\,Fe_2O_3+FeO}\right]$ of the original samples and of their fraction of 10 μ are summarized in Table 4, and the averages of these ratios for the Lower, Upper Pannonian and the Miocene, respectively, in Table 5.

The montmorillonite remains also in the deepest samples. It may be supposed that its transformation to mica was prevented because the available K^+ was not enough for this transformation [WEAWER and BECK, 1971]. The quantity of K-feldspar in these samples is too small to supply enough K^+.

However, the increase in quantities of chlorite and mica and decrease in montmorillonite and kaolinite with the depth points to a diagenetic alteration, therefore a $\frac{\text{mica}+\text{chlorite}}{\text{montmorillonite}+\text{kaolinite}}$ ratio was calculated. This ratio presumably may be characteristic of diagenetic alteration. (This ratio will be denoted with k.)

TABLE 5

Means of oxidation ratios

	Upper Pannonian	Lower Pannonian	Miocene		
			Total	Pelites	Rudites
Original samples	0,149	0,104	0,189	0,125	0,315
Fraction of 10 μ	0,581	0,346	0,378	0,372	0,390

The k values of samples are indicated in Table 4 and Table 6. The mean values of k for the Upper and Lower Pannonian and Miocene, respectively, are shown in Table 7.

Considering the means of this ratio it is found that they increase from Upper Pannonian to Miocene. This increase is only for Miocene pelites but it is not for Miocene rudites and psammites.

The correlation among k values and the types and age of the sediments is shown in Table 8.

In clay marls and aleurites k increases with the age and this increase was not found in sandstones. This fact suggests that diagenetic alterations of clay minerals did not take place at all or these alterations were restricted in the sandstones.

Fig. *2* and Fig. *3* seem to support a genetic connection between mica-chlorite and montmorillonite-kaolinite. Quantities ot kaolinite-montmorillonite decrease with the increase of chlorite-mica.

A negativ correlation might be obviously stated between mica-chlorite and montmorillonite-kaolinite and the scattering of the points between the given limits is due to the many factors influencing the genetic connections and, therefore, the distribution of the points.

TABLE 6

$\frac{Mica + Chlorite}{Montmorillonite + Kaolinite}$ (*k*) *ratio of the samples from Makó-1 drilling*

Samples	Depth	*k*
I.	805,30— 808,00	1,17
II.	1000,00—1006,00	2,86
III.	1100,50—1102,70	1,53
IV.	1200,00—1206,00	1,42
V.	1403,50—1404,05	2,68
VI.	1404,50—1405,10	2,52
VII.	1500,10—1501,50	28,47
VIII.	2150,00—2150,80	2,84
IX.	2196,00—2196,50	2,91
X.	2500,14—2500,21	3,25
XI.	2722,00—2722,35	7,09
XII.	3064,45—3064,51	6,29
XIII.	3180,15—3180,20	51,80
XIV.	3290,00—3290,20	5,33
XV.	3490,37—3490,42	2,53
XVI.	3951,83—3952,00	5,00
XVII.	4003,20—4004,35	5,04

TABLE 7

Mean values of k for Upper Pannonian, Lower Pannonian and Miocene samples

	Upper Pannonian	Lower Pannonian	Miocene		
			Total	Pelites	Rudites
Makó-1 boring	2,24	4,93			
Makó-2 boring	2,55	4,99	4,91	6,41	3,65
Means of the two borings	2,30 (10)	4,96 (19)	4,91 (12)	6,41 (6)	3,65 (6)

TABLE 8

Mean values of k for the clay marls, aleurites and sandstones

Types of rocks / Samples	Clay Marls	Aleurites	Sandstones
Upper Pannonian	1,37	2,67	2,77
Lower Pannonian	5,21	5,89	2,27
Miocene	6,41		
Mean values of each sample	5,20	4,28	2,39

There were not Miocene aleurites and sandstones in these borings.

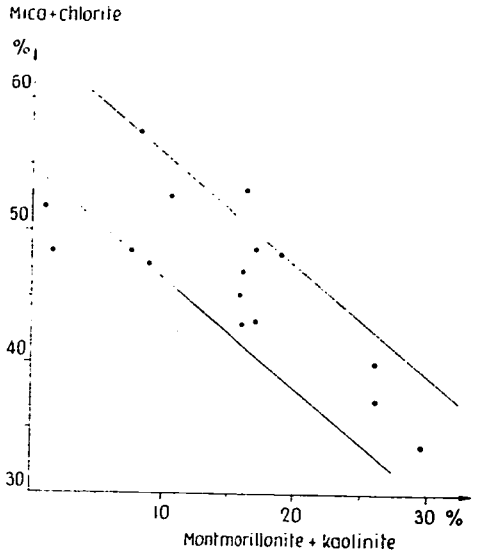

Fig. 2. Connection between mica-chlorite and montmorillonite-kaolinite contents in the samples of Makó-1 boring

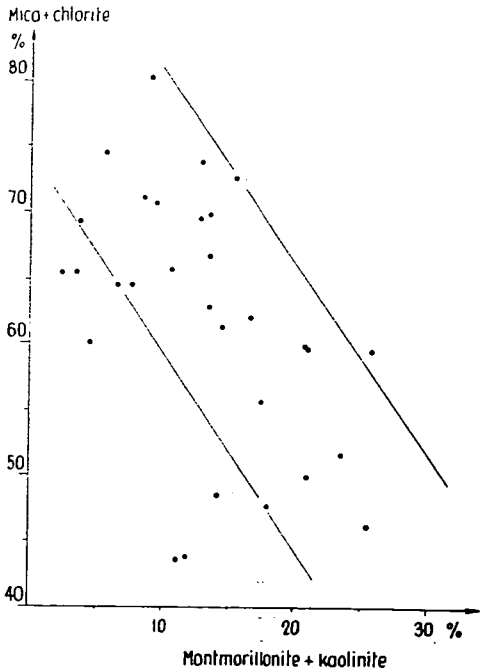

Fig. 3. Connection between mica-chlorite and montmorillonite-kaolinite contents in the samples of Makó-2 boring

Coefficients of regression were calculated on the basis of k in function of the depth for the Upper Pannonian, the Lower Pannonian and the Miocene, respectively, and they are listed in Table 9.

TABLE 9

Coefficient of regression and „a" for the Upper Pannonian and the Miocene samples

	Coefficient of regression		„a"	
	Makó-1	Makó-2	Makó-1	Makó-2
Upper Pannonian	$1{,}77 \cdot 10^{-3}$		0,91	
Lower Pannonian	$0{,}81 \cdot 10^{-3}$	$2.61 \cdot 10^{-3}$	1,88	−5,08
Miocene		$-8{,}09 \cdot 10^{-3}$		41,24
Miocene pelites		$-8{,}06 \cdot 10^{-3}$		41,24
Miocene rudites		$7{,}34 \cdot 10^{-3}$		−30,34

„a" is the $\frac{\text{mica} + \text{chlorite}}{\text{montmorillonite} + \text{kaolinite}}$ ratio extrapolated on the surface (zero m depth).

These values are positive in the Upper Pannonian and Lower Pannonian samples and negative in the Miocene ones. In the Miocene rudites the coefficient of regression is positive but this value is not to evaluate because its correlation coefficient is only 0,3.

Considering the mean values of k for the different substages and epoch mentioned, respectively, it appears that a diagenetic alteration occurred from the Upper Pannonian to the Miocene pelites (Table 7).

This is not keeping with the values of the oxidation ratios, which point to the most oxidized environment in Miocene samples (Table 5) for the oxidized environment is not favourable for diagenetic alterations.

There is no contradiction when not only the mean values of k but the coefficients of regression for the Upper Pannonian, Lower Pannonian and the Miocene are taken into account. The positive value of these coefficients suggest the above mentioned diagenetic alteration and the negative value for the Miocene shows restricted changes according to the high oxidation ratio.

Although diagenetic alterations were supposed on the basis of the distribution of the clay mineral contents these alterations can't be considered to be continuous along the depth of burial. If the k ratios were extrapolated on the zero meter depth it was found that in some cases these "a" had negative or very high positive values. This fact supports that alterations can't be taken as continuous that is in certain periods of the burial they took place and in other ones they were restricted.

SUMMARY

Core samples from the southern part of the Great Hungarian Plain were studied. Montmorillonite, kaolinite, mica, chlorite, amorphous material, quartz, K-feldspar and Na-feldspar contents were determined in the fraction of 10 μ of samples from Makó-1 and Makó-2 drillings. The quantity of these minerals changes with the depth and age and therefore diagenetic alterations may be supposed.

To characterize the diagenetic alterations a $\frac{\text{mica} + \text{chlorite}}{\text{montmorillonite} + \text{kaolinite}}$ ratio

was calculated. The average of these ratios increases with the age from the Upper Pannonian to the Miocene. The means of the ratios were calculated for the different types of rocks, too. In clay marls and aleurites this ratio increases and in sandstones it remains unchanged from Upper Pannonian to Miocene. Therefore, diagenetic alterations were supposed in clay marls and aleurites but no or restricted alterations in sandstones.

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SEDIMENTAL CORRELATIONS. A POSSIBILITY FOR THE DETERMINATION OF RELATIVE CHRONOLOGY ON THE BASIS OF THE THERMOANALYTIC (DERIVATOGRAPHIC) INVESTIGATION OF THE ORGANIC MATERIAL CONTENT OF FOSSILS

GY. SZÖŐR

ABSTRACT

The aim of the study is to propound a conceptional consideration and to call attention to the results of paleobiochemical investigations, which allow to draw the conclusion that a new procedure can be elaborated for geological epoch determinations. This statement applies to sediments embedding persistent taxons, and is valid within the limit of 30—35 million years. The author considers as taxon specific the molluscan shell and mammalian bones (fossil remainders) as an organic calcified biogenic system, in its entirety. Contrary to previous methods, comparisons of the bones and shells from different geological epochs were performed by the thermoanalytic (derivatographic) measurement of the total amount of so-called bound water and organic material.

PRESENTATION OF THE PROBLEM

The objective of the present study is to describe an assumption, and to call attention to a possibility for the elaboration of a new method that might enable us to trace the passage of geological time, or to perform the correlation of sediments that include only persistent taxons. The assumption is based on the fact that, under favourable conditions of fossilization, the conchiolin and collagen contained in molluscan shells and vertebrate bones decompose, in the geological sense, very slowly, following a well-defined law. Detailed studies on this kind of decomposition have been done in the recent past, the process was described in detail and summarized by DEGENS [1967]. The schematic decomposition process is as follows:

The initial fast aerobic decomposition of the outer soft parts is followed by the slow autohydrolysis of the organic matter contained in the shell, the end product being "free" amino acid in solvent phase or "bound" amino acid, peptide-bound, or forming metal complexes. Fossilization is completed by the dissolution of the inorganic matter of the shell, or by silica gel saturation, and recrystallization. In the course of this process, the amino acid is solved out, gets bound in the environment, or decomposes through deamination, decarboxylation. The question is whether or not the gradual decomposition of the organic matter included in the shell can be traced. Results obtained from paleobiological investigations give a positive answer. The stepwise decomposition of conchiolin has been verified by ABELSON [1955] and HARE [1966] through the estimation of the amino acid content of the molluscan shell, by TONG YUN-HO [1966] through the comparison of "shell protein—nitrogen content". GREGOIRE [1966, 1968, 1970, 1972] analysed, by electron-microscopic techniques, the shell protein of Cephalopoda, and cleared up, in detail, the diagenetic and thermometamorphic effects, at the same time theoretically verifying temporal graduality. SZÖŐR [1969, 1971*a*, 1972*a*, *b*] traced the organic matter content of the Bivalvia shell, gave a sketch of the possibility of taxonomic identification by the so-called derivatographic fingerprints, for the sake of fragmentary material identification, as

well as for facies indication and convergence determination. During his studies the latter author observed that, in the case of Bivalvial fossils enclosed in identical environment, with similar paleoecological background and exposed to solid fossilization effects (*i.e.* no recrystallization, no dissolution, no thermometamorphism), the organic material content of the shells gradually decreases with the passage of time. Naturally, the results refer to persistent taxons, to taxons displaying identical shell structures, and to comparison within one genus. The regularity was observed up to the Miocene Era inclusive, whereas the investigation of mesozoic Bivalvia shells yielded no evaluable data. The aim of the present study is to report on the results of investigations so far performed and extended to vertebrate bones and gastropod shells, as well as to sum up the results so far obtained for the Bivalvia group.

MATERIALS AND METHODS

The investigations were performed on Ophidia vertebrae, from the taxonomic category of Vertebrata, collected in karstic caves in Hungary. The geological and speleological determination of the localities has been partly completed, or is under way. The localities Bodajk and Villány-6 were reported on by KRETZOI [1956, 1964], the localities Csontos-, Vár-, Zöld caves by KORDOS [1969, 1970, 1972], the locality Porlyuk by JÁNOSSY *et. al.* [1972]. During the analysis 64 vertebrate segments were investigated by the dresent author (the samples were obtained from KORDOS). From the group Gastropoda the taxons *Cepaea* and *Planorbarius* were analysed, the samples and locality references were placed at the present author's disposal and characterized by KROLOPP [in BARTHA, 1971]. Examinations were performed on 47 shells.

The Bivalvia group (the genera *Arca, Avicula, Pinna, Mytilus, Ostrea, Cardium, Venus, Tellina, Lucina, Glycimeris, Cardita* and *Donax* altogether 380 shells, were studied in previous years by SZÖŐR [1969, 1972*a*], and detailed description of the results was given together with the data of the localities.

The sample preparation methods and the data obtained wiht the MOM type derivatograph were given account of in previous publications [SZÖŐR, 1969, 1971*b*, 1972*a*]. In the present study the essential problem is the weight per cent comparison of the materials removed by heating. Thus, in the derivatograms published here *(Figs. 1, 2, 3)* only the typical changes of the DTG-, TG curves are presented. The data of the TG curve are summarized in detail in Tables 1, 2, 3.

RESULTS

a) Investigation of Ophidia vertebrae

It is obvious from both Table 1, which summarizes the results, and from *Fig. 1,* which compares some derivatograms demonstrating the changes due to thermal effect, that the thermal losses taking place in the course of thermal analysis are as follows:

A = loss of water weakly bound to organic and mineral structures, endothermal process

B = loss of organic matter, exothermic process

C = release of carbon dioxide, due to the decomposition of the carbonate apatite structure, endothermic process

D = water released from clay minerals, endothermic process

Σ_1 = total loss of material, and Σ_2 = residue after heating.

TABLE I

Derivatographic analysis of Ophidia vertebrae, thermogravimetric [TG] conditions

Sample	Number of analyses	Age	Weight per cent values of the TG curve					
			A	B	C	D	1	2
Museological sample	2	recent	13.14	39.20	4.07	—	65.41	43.59
Zöld cave, 2 strata, Pilis Mountains	6	Holocene	7.50	15.20	3.80	—	26.50	73.50
Csontos cave, Oszoly	8	Holocene	8.80	23.40	2.52	—	34.72	65.28
Kőköz, crevice accretion, 4 strata Felsőtárkány	12	Pleistocene, Würm	6.43	7.38	7.86	—	21.67	78.33
Kőköz, crevice accretion, 1 stratum Felsőtárkány	6	Pleistocene, Riss-Würm	6.22	5.28	4.11	1.28	16.89	83.11
Kőköz, crevice accretion, 2 strata Felsőtárkány	4	Pleistocene, Riss-Würm	7.04	3.64	4.09	1.59	16.36	83.64
Porlyuk ditch, 2 strata, Jósvafő	8	Pleistocene, Riss-Würm	7.80	10.70	3.40	—	21.90	78.10
Vár cave, Budapest	6	Pleistocene, Mindel	5.02	4.35	7.02	—	16.39	83.61
Villány-6, crevice accretion, Villány Mountains	2	Pleistocene, Mindel	6.74	2.61	3.80	2.61	14.02	85.98
Bodajk, crevice accretion, Vértes Mountains	6	Middle Oligocene	4.96	2.38	3.51	1.86	12.71	87.29

A = water bound to organic and mineral structure,
B = organic matter
C = CO_2 released from carbonate apatite, D = water bound to clay minerals
1 = total loss of material, 2 = residue after heating

It is striking that the organic matter content gradually decreases depending on the length of the period of embedding. Inconstistent with this trend is the sample material from two strata of Porlyuk ditch with the high value of 10.70 %. With the other forms of material loss, *i.e.* loss of water, release of carbon dioxide, total loss of material and residue after heating no such correlation can be observed. It is noteworthy that on the samples collected from several localities clay mineral formation can be observed. The clay mineral, in our opinion, is no structural component of the bone material, but an impurity filling up the cracks. Very naturally, in this case, in connection with the loss of water (denoted by A), the release of OH bound to clay mineral must also be taken into account.

b) Investigation of Gastropod shells

It was also observed in the study on gastropod shells, in consistence with the previous results form studies on Bivalvia shells that if embedding is young, a taxonomic difference can be pointed out (derivatographic fingerprint up to the level of genus, SZÖŐR, 1972*a*). The derivatographic image (fingerprint) of the genus Planorbarius differs noticeably in the given geological time interval. During the study of the species Planorbarius, material losses A, B and C were observed, whereas the species

Cepaea considerably differs by the occurrence of the material loss O. The results are summarized in Tables 2 and 3, and illustrated in *Figs. 2* and *3*. In the Figures only the thermal reactions up to 700 °C are presented, since great-scale release of carbon dioxide (C) can only be measured by another way of programming. Consistent with

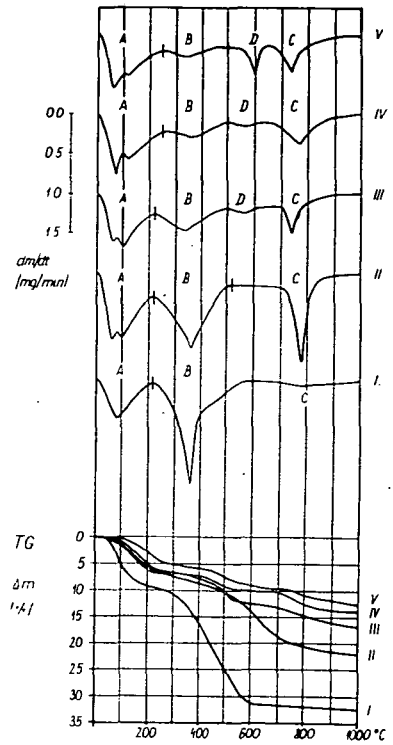

Fig. 1. Derivato-thermogravimetric (DTG) and thermogravimetric (TG) analysis of *Ophidia* vertebrae
I = Holocene (Oszoly), II = Pleistocene, Würm (Felsőtárkány), III = Pleistocene, Riss-Würm (Felsőtárkány), IV = Pleistocene, Mindel (Villány-6), V = Middle Oligocene (Bodajk), A = release of water bound to organic and mineral structure (endothermic) B = release of organic matter (exothermic), C = release of carbon dioxide from the carbonate-apatite structure (endothermic), D = release of water bound to clay mineral (endothermic)

those previously described is the interpretation of columns A and B, the C values denote the amount of carbon dioxide released from calcium carbonate. The material loss denoted by O has not yet been exactly defined, it may consist either in the loss of water enclosed in the aragonite structure [HUDSON, 1967] or in the burn-out of organic matter or perhaps the sum of both. Burn-out of organic matter is the easiest to prove. It is well-known that in the shell of the species Cepaea a pattern built up of organic material can be seen. A similar material loss was observed during the examination of the species Neritina, the shell of which similarly displays some pattern [SZÖŐR, 1971*a*]. The DTA curve (not shown in the Figure) also indicates a slight exothermic slope. This is why in the Table the value O is assigned to the value B, and the amount of organic matter is compared with the value B+O.

TABLE 2

Derivatographic analysis of shells of the species Planorbarius, thermogravimetric /TG/ conditions

Sample	Number of analyses	Age	Weight per cent values for the TG curve				
			A	B	C	Σ_1	Σ_2
Planorbarius corneus (L), Bratislava	6	recent	0.4545	2.3636	40.8183	43.6364	56.3636
Planorbarius corneus (L), Sárrét	6	Holocene	0.4546	1.3182	40.9545	42.7273	57.2727
Planorbarius corneus (L), Tószeg	4	Pleistocene	0.4009	0.8726	40.2359	41.5094	58.4906
sp. *Planorbarius*, Várpalota	5	Upper Pannonian	0.3846	0.7692	40.2247	41.3785	58.6215
Planorbarius cornu manteli, (DUNK) Öcs	7	Upper Pannonian	0.3714	0.7749	40.2113	41.3576	58.6424

A = water bound to organic and mineral structure
B = organic matter
C = CO_2 released from calcium carbonate
Σ_1 = total loss of material
Σ_2 = residue after heating

With both species the amount of organic matter (sp. Planorbarius in Table 2, column B; sp. Cepaea — Table 3, column B+O) gradually decreases depending on the length of the embedding period. Such a correlation cannot be established by measuring the amount of released water or carbonate. Unlike the case of Ophidia vertebrae, the total loss of material (Σ_1), and residue of heating (Σ_2) values — inversely proportional to each other — are in correlation with the period of embedding.

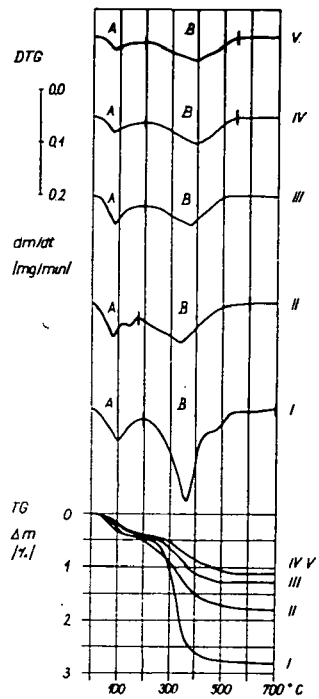

Fig. 2. Derivato-thermogravimetric (DTG) and thermogravimetric (TG) analysis of several species of *Planorbarius*
I=Recent (Bratislava), II=Holocene (Sárrét) III=Pleistocene (Tószeg), IV, V=Upper Pannonian (Öcs, Várpalota), A=release of water bound to organic and mineral structure (endothermic), B=release of organic matter (exothermic)

SUMMARY OF RESULTS. CONCLUSIONS

All that have been described so far unequivocally prove that the amount of organic matter detectable in gastropod shells and vertebrate bones gradually decreases with the passage of geological time. This statement is supported by a similar conclusion drawn previously in connection with Bivalvia shells. *Fig. 4* serves to demonstrate this regularity. Here the organic matter content of the shells or bones of the taxonomic groups under study (weight per cent values) is compared with the geological age and the period of embedding.

The curve referring to Bivalvia shells, naturally, is interpreted in a global way, since it sums up the mean values for a number of genera. In this sense, it characterizes only the fossilization, the stepwise organic matter loss of the marine, littoral-sub-

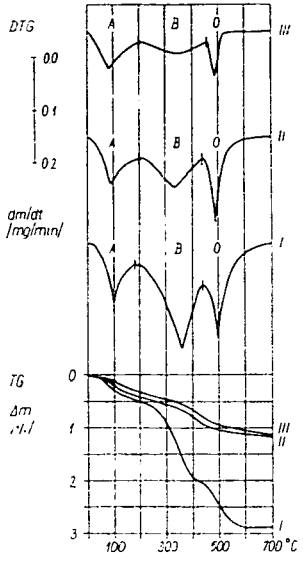

Fig. 3. Derivato-gravimetric (DTG) and thermogravimetric (TG) analysis of several species of *Cepaea*
I=Recent (museological sample), II=Pleistocene, Mindel (Vértesszőlős), III=Miocene (Mainz), A=release of water bound to organic and mineral structure (endothermic), B and O=loss and burn-out of organic matter in two steps (exothermic)

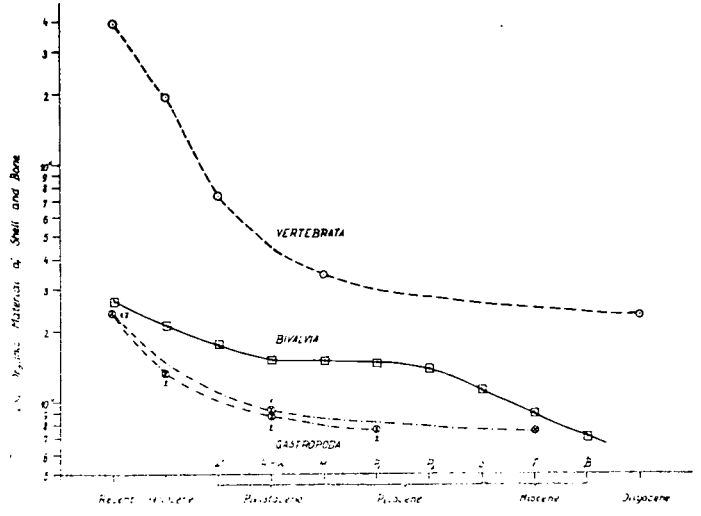

Fig. 4. Loss of organic matter in vertebrate bones, gastropod and Bivalvia shells depending on embedding time
Vertebrata=Ophidia vertebrae (64 samples), *Bivalvia*=genera: Arca, Avicula, Pinna, Mytilus, Ostrea, Cardium, Venus, Tellina, Lucina, Cardita, Donax (380 samples), *Gastropoda*=1) genus Cepaea, 2) genus Planorbarius (47 samples), W=Würm, R—W=Riss—Würm, M=Mindel, P_1=Upper Pliocene, P_2=Lower Pliocene, S=Sarmatian, T=Tortonian, B=Burdigalian

TABLE 3

Derivatographic investigation of shells of sp. Cepaea, thermogravimetric [TG] conditions

Sample	No. of analyses	Age	Weight per cent values of the TG curve						
			A	B	O	B+O	C	Σ_1	Σ_2
Cepaea vindobonensis (FÉR.), museological sample	6	Recent	0.4893	1.5902	0.7951	2.3853	41.7737	44.6483	55.3517
Cepaea vindobonensis (FÉR.), Vértesszőllős	6	Pleistocene	0.2602	0.5004	0.4003	0.9007	42.0737	43.2346	56.7654
Cepaea subglobosa ( ), Mainz	6	Miocene	0.3670	0.5505	0.2294	0.7799	41.9723	43.1192	56.8808

A = water bound to organic and mineral structure
B and O release and burn-out of organic matter in two steps
C = CO_2 released from calcium carbonate
Σ_1 = total loss of material Σ_2 = residue after heating

littoral biotope, shellfish population embedded in silty sand. It calls attention to the fact that there is a possibility for such a categorization and summarization in the case of a great number of sample materials.

The investigation on Ophidia vertebrae proves that the measurement as well as the comparison of organic matter through the derivatographic method can be performed also with bone material. This fact has been theoretically verified, with reference to historical periods, by DÁVID [1969] and KISZELY [1969] through the derivatographic study of subfossil human bones. The apatite structure that builds up the bones contains significantly more organic matter than the calcite- and aragonite-containing shell. Even vertebra segments embedded in cave sediments from the Pliocene enclose more organic matter than recent molluscan shells (without the periostracum). It should be mentioned here that the similar examination of tooth material, in view of the extremely high resistance of the dental enamel, promises even more favourable results.

When describing the results, mention was made that the material from a single cave (Porlyuk ditch, 2 strata, Jósvafő) does not fit in with the trend of organic matter decrease. The organic matter content of 10.70%, denotes a much younger time of embedding (Holocene), instead of the present chronological assignment (Pleistocene, Riss-Würm). This facts sets us an objective to study the given formation in fuller detail.

The organic matter content of Cepaea and Planorbarius shells is even less than that of Bivalvia shells. The difference observed on corresponding recent species gets even more pronounced during fossilization. The thin shell of snails made up of aragonite gets more damaged than the thicker calcite and calcite-aragonite-containing shells of shellfish. In spite of this, the taxonomic specificity observable on the genus level can be established, and this gives a basis for chronological comparison.

To go back to the original concept, the essentials can be drawn up as follows:

The fossilization of shells, snail-horns, bones can be traced and graded. The residual organic matter content, as a well-defined measure, can characteristically reflect the passage of time. Such an assessment of time, very naturally, belongs in the field of relative chronology, but obviously can be applied to settle the given problem. Such problems may be the fine levelling, chronological description of a sedimental conglomerate, its correlation to the similar ones, which can be hardly or not at all performed either on the grounds of the properties of the lithofacies (uniform sedimental conglomerate), or the properties of the biofacies (persistent fauna). In such investigations the most essential requirement is that the comparison be performed within a given taxonomic group — in ideal cases on the genus level. Examinations can be performed only on fossil samples that have not been crystallized, imbued or exposed to metamorphic effects. If molluscan shells are available as fragment material (lumasella) — particularly when analysing samples from bores — the work begins with structural analysis by optical methods [BØGGILD, 1930; OBERLING, 1964; TAYLOR *et al.*, 1964, 1973]. Organic matter content is determined through the derivatographic measurement of the thus defined fragment materials of identical structure.

Furthemore, it can be expected that in the case of Holocene, Pleistocene, Pliocene fossils, on the grounds of the evaluation of a great number of samples, through the statistical evaluation of the results and organic matter measurement, an absolute chronology can be established.

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GEOHISTORICAL EVOLUTION AND DOLOMITE SEDIMENTATION OF THE NATRON LAKES OF FÜLÖPHÁZA, KISKUNSÁG NATIONAL PARK, HUNGARY

B. MOLNÁR and I. M.-MURVAI

INTRODUCTION

The origin of the natron lakes of the southern Great Plain of Hungary has been studied for more than a decade by a working team of geologists, biologists, hydrochemists and geographers. After the scientific elaboration of several natron lakes of the area, now a new research project concerning the natron lakes of Fülöpháza has been launched *(Fig. 1)*. The area of the lakes is a part of the Kiskunság National Park, very important geologically, being situated along the highest belt of the Danube-Tisza Interfluve's sand ridge, on its eastern side sloping towards the Tisza river, there, where wind-blown sands are still in motion, affected very little, if at all, by man's intervention.

The geological investigation of the Fülöpháza lakes has been aimed at contributing to the knowledge and understanding of the origin and evolution of the lakes and of the lacustrine sedimentary sequence deposited there.

LATEST QUATERNARY HISTORY OF THE DANUBE-TISZA INTERFLUVE

The natron lakes of Fülöpháza occur on the wind-blown sand ridge of varied topography between the rivers Danube and Tisza. The territory of Hungary, consequently, that of the Danube-Tisza Interfluve as well, belonged, in the Pleistocene, to the periglacial climatic zone. Its evolution was controlled by two main faktors: on one hand, the alternation of markedly warm and cold phases due to the presence of the Pleistocene periglacial zone and the subsequent warmer climatic effects of the Holocene; on the other hand, the basin-shaping effect of tectonic movements controlling both the size and rate of accumulation and the particular sedimentary facies of the subareas.

Not every part of the Great Hungarian Plain did subside at the same rate in the Quaternary. For instance, the Danube seems to have flowed, up to the Günz-Mindel Interglacial, across the present-day Interfluve area diagonally towards the city of Szeged in the southeast [I. MIHÁLTZ, 1953; B. MOLNÁR, 1961, 1967, 1970, 1972, 1973; M. KRETZOI, E. KROLOPP, 1972; E. KROLOPP, 1970]. In the Günz-Mindel Interglacial, however, the Danube-Tisza Interfluve subsided at a lower rate compared to the adjacent areas; in fact, it may have uplifted a little. The present-day Danube valley, however, underwent a tectonic subsidence and this movement forced the Danube to abandon its diagonal course and occupy its present-day meridional valley.

Over the rest of the Pleistocene the Danube-Tisza Interfluve was not involved in fluviatile accumulation and a dry land topography developed on its surface.

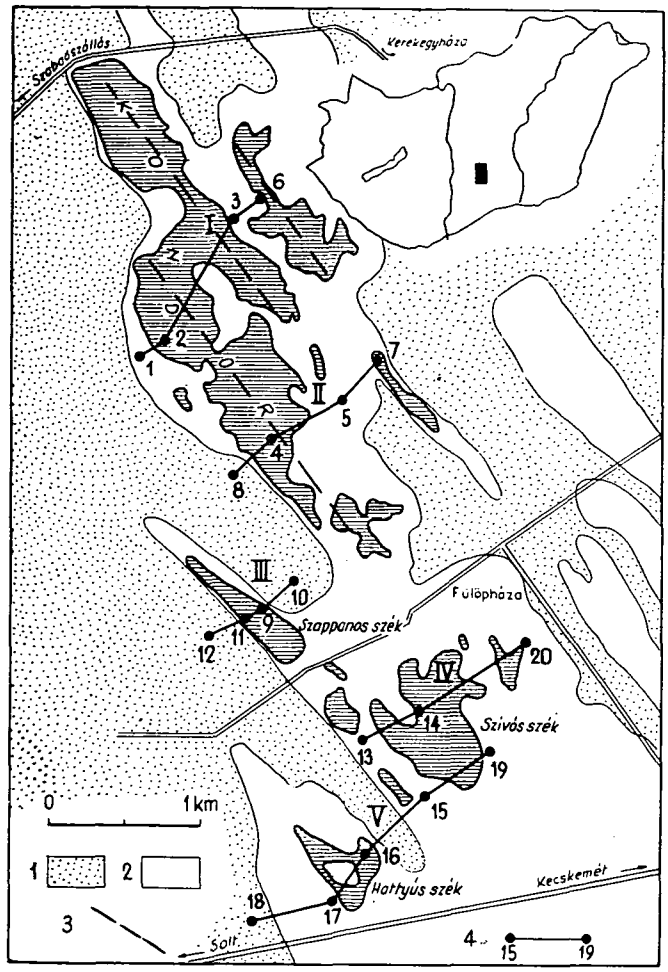

Fig. 1. Layout of the natron lakes of Fülöpháza with borehole dots and locations of geological profiles

1. Wind-blown sand area, *2.* Area filled up with lacustrial sediment, *3.* Axes of the one-time depressions of Lake Kondor, *4.* Locations of boreholes and geological sections

The westerly winds of the cold spells which introduced the glaciations blowed out sands from the flood-plain of the Danube depositing them as aeolian sands on the surface of the ridge. During the glaciations, loess was formed on the wind-blown sand surface. Alternating with wind-blown sand, loess attains 150 m thickness in some places in the middle part of the Danube-Tisza Interfluve, reaching up to the present-day surface [B. MOLNÁR, 1961]. Thus the surface of the Danube-Tisza Interfluve is covered predominantly by these formations.

In the Holocene the deposition of gravels, which had begun in Pleistocene time, continued in the Danube valley. In several places the surface of the gravel sheet was overlain by allochtonous loess, in other places, by peat accumulated in considerable thickness.

On the Danube-Tisza Ridge, morphologically a land surface elevated 30 m high above the Danube valley floor and almost 40 m above the Tisza's alluvium, the predominant winds of NW—SE direction arranged, in the summer half-year, the windblown sands in NW—SE trending dune ranges, particularly so in the dry hazelnut phase of the Holocene when the ground-water table lay considerably deeper than today. Between the sand dunes NW—SE trending hollows developed corresponding to the wind direction predominating in summer. It is these hollows that enabled in the Danube-Tisza Interfluve area the development of shallow-water lakes, those of Fülöpháza inclusive *(Fig. 1)*. Most of the lakes extend in NW—SE direction corresponding to the trend of the sand dune ranges.

GEOLOGICAL FORMATION OF THE LAKES OF FÜLÖPHÁZA

The natron lakes of Fülöpháza too are situated in NW—SE trending hollows of wind-blown sand environment. Largest and of most permanent water cover of all the lakes is Lake Kondor, 3 to 4 km long and 1.0 to 1.5 km wide. The rest of the lakes are of substantially smaller size and it is only Lake Szappanosszék that does not dry out for a considerable length of time, just like it is the case with Lake Kondor. All lakes but Szappanosszék vary in size from season to season, the more so, their size is even dependent on rainfall, showing a swift increas in years of striking humidity. Morphologically, the Szappanosszék is bounded by such relatively higher wind-blown sand-dune ranges between which there are narrow hollows, so that the possibility for

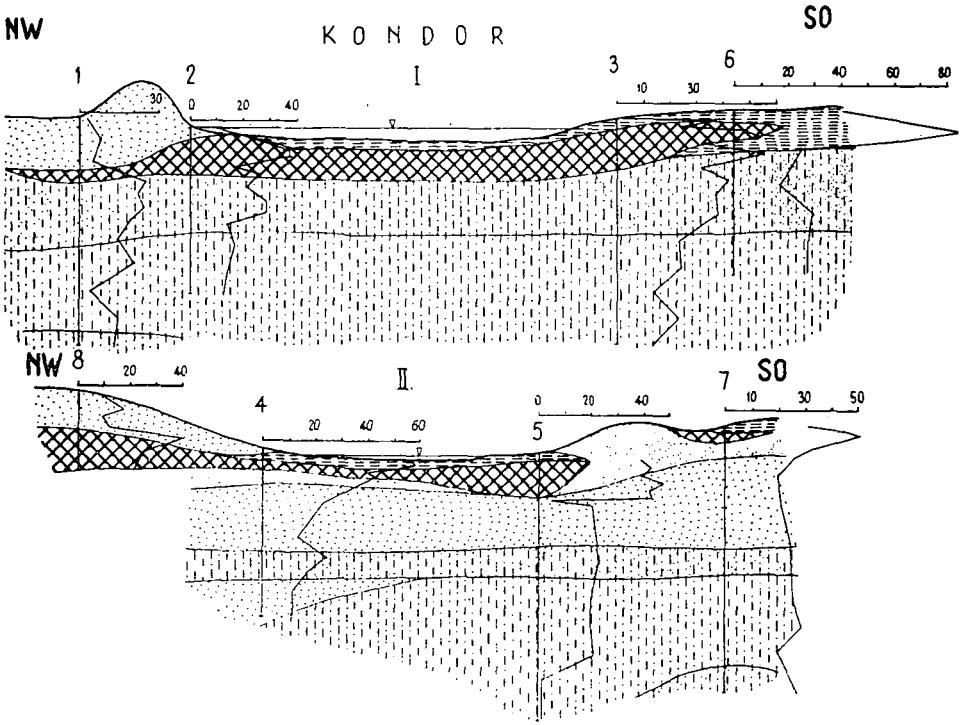

Fig. 2. Geological sections of Lake Kondor (For legend, see *Fig. 3.*)

changes in the size of the lake water table is rather restricted. Lakes Hattyússzék and Szívósszék run completely dry in the summer half-year.

The results of wind action there are indicated by the emplacement and shape of the depressions enclosing the lake-water bodies as well as by the intrusion of the sand dune ranges from northwestern direction into the hollows just mentioned (see *Fig. 1*).

In the neighbourhood of the lakes the authors carried out on-the-spot observations, then they collected rock samples. 5- to 10-m-deep holes were drilled into the ground in the vicinity of the lakes. The samples recovered were hydrometrically analyzed for grain size distribution, then the carbonate content in terms of $CaCO_3$ and, in some cases, the humus content of the camples were determined. In some boreholes the ground-water hit by drilling was sampled and the chemical composition of the water was compared with that of Lake Szappanosszék's water containing the highest quantity of dissolved solids.

On the basis of the results thus obtained, the geological map of the area was drafted and the lithological logs of the boreholes were grouped into geological sections *(Fig. 1—3)*.

The geological sections include three main sedimentary sequences over the depth range thus far penetrated.

1. The lower part of the sequences is constituted by predominantly Pleistocene fine-sandy loesses.

2. The fine-sandy loesses are overlain by a diversified development of sediments of coarser grain size in the majority of the places (fine to small sands).

3. This coarser sedimentary sequence, at Szappanosszék the loesses directly, is overlain by lacustrial sediment, mainly carbonate silt.

In the course of a detailed analysis of these sediments the following observations have been made.

(1) The oldest sediment reached by drilling in the survey area is fine-sandy loess. Its deepest subsurface position is in Section II of Lake Kondor, at 5 m or so, the position closest to the surface, at 2 m depth, being at Szappanosszék. The boreholes have penetrated the fine-sandy loess in 4 to 5 m thickness on the average. The largest thickness uncovered, 7 m, was in borehole Hattyússzék-18. The loess is fine-sandy throughout the area, the fine sand content showing a wide range of variation. Its grain size composition has been examplified by curves C and D in *Fig. 4*. As can be read off from these curves, the share of fine and small sands combined attains 30 to 35% on the average in the loess: a considerable quantity compared to the loess so far examined from the Danube-Tisza Interfluve area. The sorting of the loess is poorer than in other parts of the Interfluve.

All the above are due to the fact that at the time of loess formation the area must have been, like it is the case at present, morphologically more diversified as compared to the rest of the Danube-Tisza Interfluve. The surface of wind-blown sands underneath was duned, so that the finer fraction of the wind-blown sands has been admixed to the loess. That the land surface had a varied relief at the time of loess deposition is evidenced by the fine-sandy layer reached in the loess in a number of places, *e.g.* in borehole Nr. 1 of Section I of Lake Kondor, borehole Nr. 7, Section II, and borehole Nr. 17, Section V, Hattyússzék. These fine-sandy beds testify to convex landforms, while the dark grey silts of 16.0% humus content with plenty of gastropod shell remnants, deposited on a water-covered loess surface and now recovered by borehole Nr. 15 or Nr. 18, Section V, Hattyússzék, in fact, the carbonate silt underneath, are evidences of concave surface landforms *(Fig. 2, 3)*.

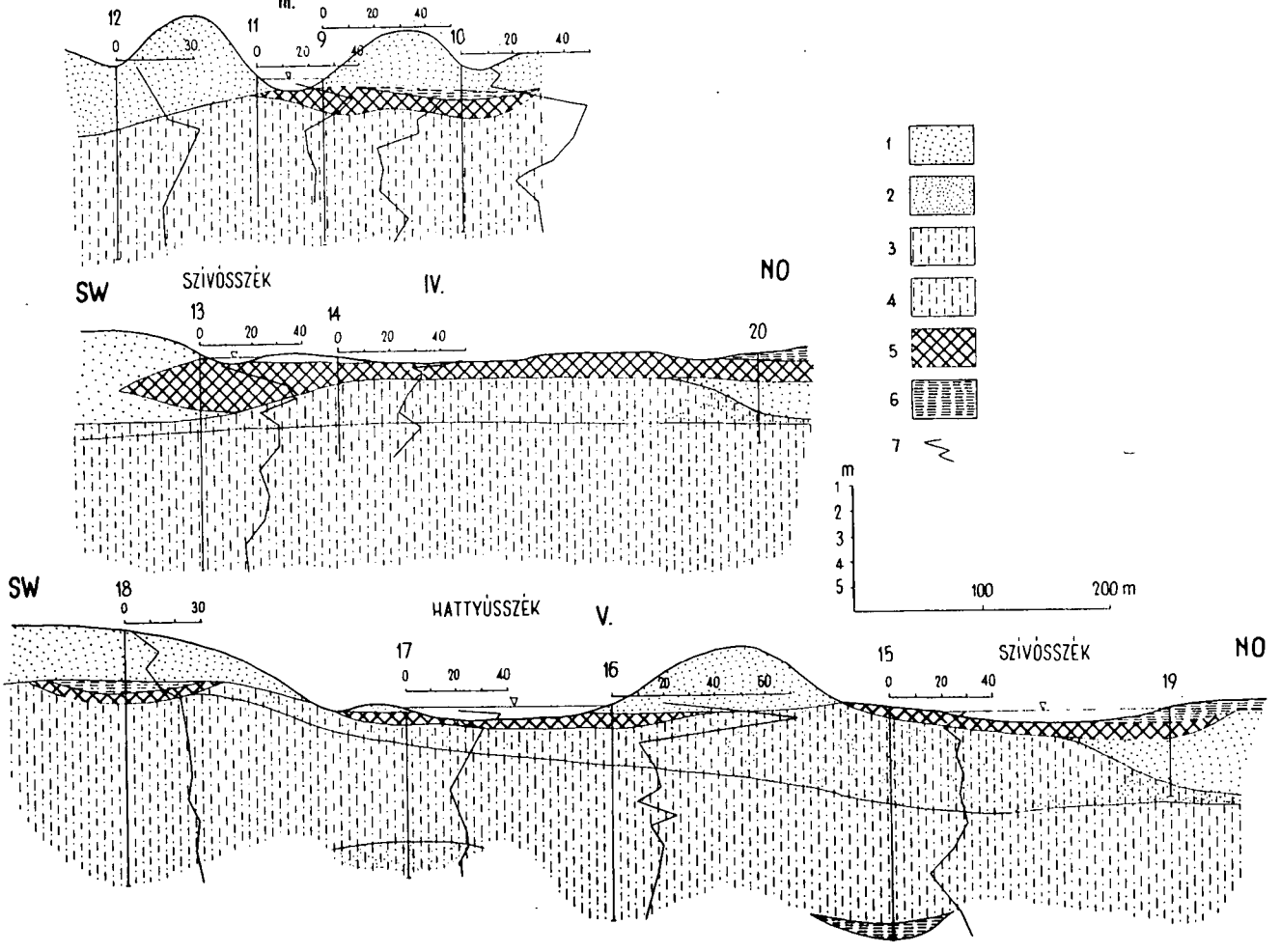

Fig. 3. Geological sections of the Szappanosszék, Szívósszék and Hattyússzék
1. Small-grained wind-blown sand (0.1—0.2 mm), 2. Fine sand (0.06—0.01 mm), *3.* Loessic fine sand (0.02—0.1 mm), *4.* Fine sandy loess (0.02—0.1 mm), *5.* Carbonate silt, *6.* Heavily humic, unsorted silt (0.005—0.1 mm), *7.* Carbonate %.

The fine-sandy loesses are of porous structure and because of their position below the ground-water table, where reduction processes are in action already, they are of grey colour in the majority of the places.

The carbonate content of the fine-sandy loesses is considerable in all but a few samples, averaging between 25 and 30%. In some cases, however, particularly there,

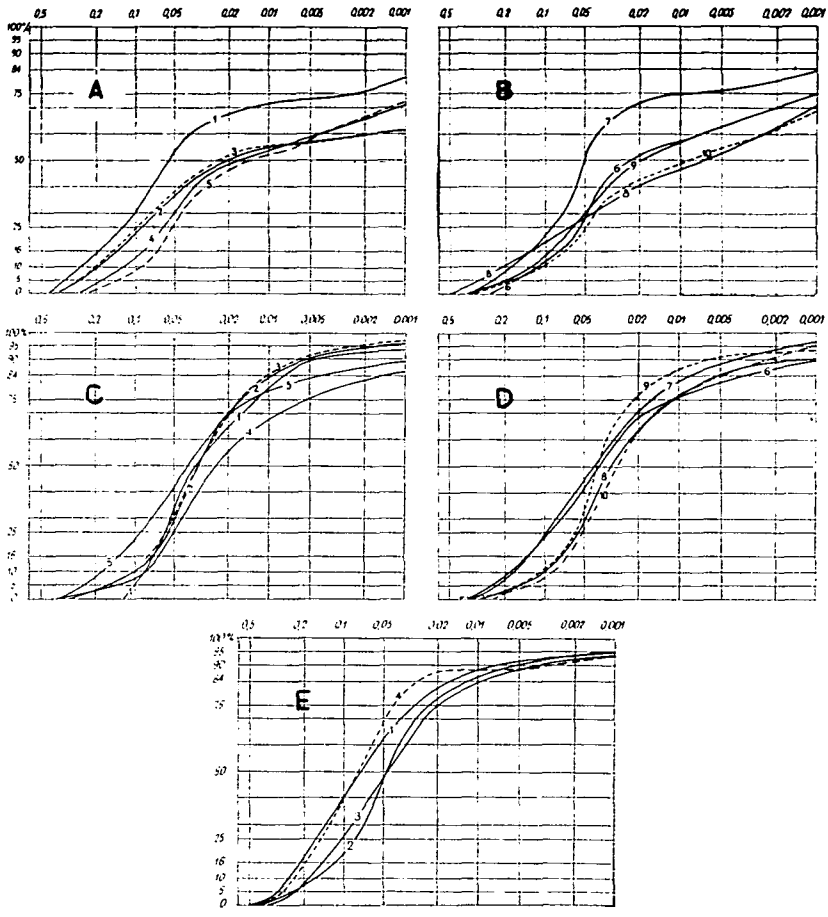

Fig. 4. Curves of grain size composition types of major types of sediment deriving from the area of the natron lakes of Fülöpháza, with the carbonate content of the samples

A—B Granulometric curves of carbonate silt samples
1) Lake Kondor, borehole No. 1 2.0—2.5 m (26.0%)
2) Lake Kondor, borehole No. 2 0.5—1.0 m (36.4%)
3) Lake Kondor, borehole No. 2 1.0—1.3 m (36.4%)
4) Lake Kondor, Borehole No. 3 0.3—0.4 m (50.0%)
5) Lake Kondor, borehole No. 3 0.4—0.5 m (48.0%)
6) Lake Kondor, borehole No. 3 0.5—0.6 m (57.0%)
7) Lake Kondor, borehole No. 3 1.0—1.5 m (50.0%)
8) Lake Kondor, borehole No. 6 0.6—0.8 m (72.0%)
9) Lake Kondor, borehole No. 4 0.4—0.5 m (56,5%)
10) Lake Kondor, borehole No. 5 0.2—0.4 m (65.5%)

where overlain by a carbonate silt layer, the loess is even richer in carbonate (*Fig. 3,* Section III, borehole Nr. 11, *Fig. 4,* D). At the last-mentioned occurrence, the part ex-solved from the carbonate silt layer has been accumulated by downward-migrating waters.

(2) In all places, excepting Section III, Szappanosszék, the fine-sandy loesses are overlain first by loessic fine sands grading into unconsolidated, smallgrained, wind-blown sands.

Within the survey area examined, the thickness of the loessic fine sands varies between 0.5 and 2.8 m, that of the small-grained sands between 1.0 and 3.5 m. The average thickness is, accordingly, 2.6 to 6.0 m or so.

The fine- to small sand content of the loessic fine sands attains, or even exceeds, 50%. Consequently, the finer fraction too is represented in substantial quantity in them (*Fig. 4,* E).

The predominant fraction of the small-grained wind-blown sands is between 0.1 and 0.2 mm. In the wind-blown sand area lying west of the lakes, however, interbedded wind-blown sand lenses of 0.4 to 0.8 mm predominant grain size, heavily rounded, of dull surface, can frequently be encountered.

The loessic fine sands largely vary in carbonate content, this variation being primarily dependent on the availability of carbonate silt above them. If there is any, the carbonate content attains even 25 to 30%, if not, it is as low as 15% or so.

As shown by earlier examinations of heavy minerals, the sands occurring here have been deflated from the flood-plain of the Danube in the west, thus being of Danubian origin [B. MOLNÁR, 1961].

It is characteristic of the loessic fine sands that they lie parallel to the fine sandy loess layer, growing thicker to varying extent and not pinching out over considerable distances and showing an upward increase in grain size.

The small wind-blown sand is arranged in dunes and accordingly the greatest thickness of the sand layer can always be measured in the vertical plane traceable from the top of the dune downwards. The wind-blown sand will often pinch out.

(3) The youngest sediment of the area is represented by lacustrial carbonate silt and palustrial silt. According to composition and origin, the carbonate silts can be split up into three groups:

a) The lower part of the carbonate silt derives from waters infiltrating deepwards and percolating across beds of higher carbonate content atop. This makes

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C—D Granulometric curves of fine sandy loess
1) Lake Kondor, borehole No. 1 6.0—7.0 m (5.0%)
2) Szappanosszék, borehole No. 12 2.5—3.0 m (32.7%)
3) Szappanosszék, borehole No. 12 3.0—3.5 m (28.6%)
4) Szappanosszék, borehole No. 11 1.0—1.5 m (31.4%)
5) Szappanosszék, borehole No. 11 1.5—2.5 m (19.0%)
6) Szappanosszék, borehole No. 9 1.5—2.0 m (36,4%)
7) Szappanosszék, borehole No. 9 3.0—4.0 m (23.0%)
8) Szappanosszék, borehole No. 9 5.0—6.0 m (34.1%)
9) Hattyússzék, borehole No. 18 3.0—5.0 m (25.4%)
10) Hattyússzék, borehole No. 18 9.0—10.0 m (30.4%)

E: Granulometric curves of fine sands
1) Lake Kondor, borehole No. 1 4.0—5.0 m (14.5%)
2) Lake Kondor, borehole No. 2 3.5—4.0 m (15.0%)
3) Lake Kondor, borehole No. 6 2.0—2.5 m (20.4%)
4) Szívósszék, borehole No. 14 0.0—0.5 m (25.0%)

up 30% or even more of the total thickness of the carbonate silt; thus being about 0.3 to 0.4 m thick, though largely varying in thickness even within one and the same lens. In other Interfluve natron lakes studied earlier this thickness was more considerable. For instance, in the case of Lake Kerek of Bugac it attained 0.6 to 0.8 m [B. MOLNÁR, M. SZÓNOKY 1974].

The infiltrating, carbonate-rich solution impregnated the basal, fine to small sands or, at Szappanosszék, the loess, and it was primarily the pores of the rock that were filled up by the precipitated carbonate matter. The transition upward into the middle member is without any remarkable or sharp limit. The carbonate content is largely variable, usually 25 to 50% or so, being heavily dependent on the quantity of water migrating deepward and laterally, a quantity remarkably controlled and influenced by the morphology of the land surface. The lower member is distinguished from the middle one by the higher amount of the fraction insoluble in hydrochloric acid, too. Its insoluble residue consists primarily of fine to small sands or, at Szappanosszék, of a material corresponding in grain size to the loess fraction.

b. The middle part of the carbonate silt attains as a rule 50 to 60% of the total carbonate silt thickness, being 0.6 to 0.8 m thick.

Because of the increasing precipitation of carbonate here, the carbonate content is often as high as 70 to 80%. Although it does not always attain this figure, it is above 50% in the majority of the cases, however. The composition of the insoluble residue is similar to that of the lower part, but its quantity is considerably smaller. When dry, this sediment is white to greyish-white and of loose structure. Its composition and characteristics were shown in detail, and its distribution in the Interfluve area described, in earlier works [I. MIHÁLTZ, M. FARAGÓ, 1946; M. MUCSI, 1963; B. MOLNÁR, 1970, 1971; B. MOLNÁR, M. SZÓNOKY, 1974]. As shown by the *X*-ray diffraction results of P. KRIVÁN and E. NEMECZ, the carbonate silts of the Danube-Tisza Interfluve were identified as being of lime and dolomite composition [in P. KRIVÁN 1953]. The carbonate silt contains molluscs only quite unfrequently, and even if so, the forms available represent only one or two species.

c. The upper member of the carbonate silt accounts for 10 to 15% of the total carbonate silt thickness, i.e. 0.1 to 0.2 m. Its carbonate content is lower than that of the middle part, being similar to that of the lower one, hence 25 to 50% or so. Characteristically enough, it is laid down in those parts of the natron lakes which are water-covered for the longest span of time. The difference from the lower and middle members consists in that the clay content in its insoluble residue is higher than in the other two members. The result is that the sediment is heavily cracked upon dessication, the cracks penetrating to a depth of 6—8 cm.

In the plotted geological profiles the subdivisions of the carbonate silt have been omitted for technical reasons, so that the carbonate silt bed shown on the profils includes all three members just quoted *(Fig. 2, 3)*. As can be readily seen on the profiles, the carbonate content extends beyond the present-day boundary of the lakes. Moreover, there are such buried carbonate silt lenses which are not interconnected with the carbonate silt of the lakes (*Fig. 3,* borehole 18). Since carbonate silt is deposited only at permanent water coverage, the extension of the lakes must have been other than today, several minor lakes having been buried by wind-blown sands in the meantime.

Examples on the grain composition of the carbonate silt have been shown in curves A—B of *Fig. 4*. It is evident that every sample contains sands in considerable, but subequal, quantity. Their fine silt and clay fraction, however, shows a much wider fluctuation (0.002 mm $\varnothing >$). Notably, the quantity of the fine fraction in the

carbonate silt depends on the value of the carbonate content in it and on whether the upper, more argillaceous, part or the two other members have been sampled.

d. In those points of the lakes, where the vegetation is or was more lush compared to the rest, *e.g.* in the reed-grown zones, 0.1 to 0.3 m of heavily peaty-earthy, ill-sorted sandy silts, rich in gastropodes, can be found. Such a layer occurs, *e.g.*, in profiles I and II of Lake Kondor *(Fig. 2)* and in boreholes 10 of profile III and borehole 15 of profile V. This layer contains lacustrial deposits and a mixture of fine and small-garined sands blown by the wind into the lake ,combined. This accounts for the poor sorting, too.

GEOHISTORICAL HISTORY OF THE NATRON LAKES OF FÜLÖPHÁZA AND DEPOSITION OF SEDIMENTS IN THEM

It is generally agreed on that the uppermost loess horizon reached by drilling in the Danube-Tisza Interfluve represents the end of the Pleistocene, i.e. the Würm III glaciation. As shown in the above, the loess of the Fülöpháza region is represented by fine sands grading upwards into loessic fine sands in the majority of the places. Similar latest Pleistocene sequences were observed in a number of places by I. MIHÁLTZ and L. MOLDVAY [in I. MIHÁLTZ, 1953] as well. As already pointed out, the loess matter could have been deposited and generated on a surface of varied topography and morphology.

Accordingly, the sedimentary sequence overlying the fine sandy loess or the loessic fine sand is already of Holocene age. The chronology of the deposition of the Danube-Tisza Interfluve's Holocene sequence is well-known thank to contributions by I. MIHÁLTZ, M. M-FARAGÓ [1964], B. ZÓLYOMI [1953], A. HORVÁTH, S. ANTALFI [1954], M. MUCSI [1963, 1965, 1966], M. M.-FARAGÓ [1966, 1969], M. ANDÓ, M. MUCSI [1967]. They too believe that the fine sandy loess and loessic fine sand of the Fülöpháza region developed in the late glacial phase and that the sedimentary sequence overlying it represents the post-glacial period already.

On the basis of pollen grains and gastropodal fauna the afore-mentioned authors have subdivided the post-glacial period into the following stages: birch-pine, hazelnut, oak and beech. These stages correspond to FIRBAS's IVth to IXth climatico-vegetational phases [FIRBAS, F. 1949].

According to the above, the fine sandy loess and loessic fine sand uncovered at the base of the profiles must have been deposited during the Würm III glaciation. The wind-blown sand sequence overlying the loessic fine sand thus began in the birch-pine stage. Some of the lakes, e.g. the Szappanosszék, the NW part of Lake Kondor and the Hattyússzék, existed at the beginning of the Holocene already. Notably, the carbonate silt in these directly overlies the loessic fine sands or the fine sandy loess. In other cases, *e.g.* in that of the SE part of Lake Kondor, it was formed probably later, in the place of a depression that had existed in the hazelnut stage already, in the first half of the more humid oak stage.

The difference between the two parts of Lake Kondor is due to the fact that the presentday configuration of the lake was shaped by the fusion of two or three parallel depressions. This is evident from *Fig. 1,* too. The formation of similar, so-called H-shaped, lakes was already mentioned by F. SMAROGLAY [1939]. According to that author, in cases like that the dune range between two adjacent depressions is broken through and a communication is established between them. In the present case Lake Kondor was brought about by three parallel depressions. Accordingly, the

flats in this lake type are formed at different times and under different circumstances, hence their dissimilar basement and bottom morphology.

Understanding of the mechanism of lacustrial carbonate silt deposition and precipitation has been greatly enhanced by earlier investigations by A. HORVÁTH [1950], P. KRIVÁN [1953], T. NÓGRÁDI [1956], Zs. DVIHALLY [1970], J. SZÉPFALUSI [1970] and A. RICHNOVSZKY [1970]. Complementing their results and taking into consideration the geological processes and circumstances, we can explain the origin and deposition of the carbonate silt in the following way.

The lakes are recharged by meteoric waters and ground-water flowing toward local depressions. Particularly, the recharging effect of ground-water is of importance. The precipitations falling into the lakes of the Danube-Tisza Interfluve and the waters getting from surface watercourses into the lake are less in quantity than the annual rate of evaporation. Thus the excess of water seems to derive from the ground-water resources [M. ANDÓ, 1964].

The sand of Danubian origin making up the basement of the lakes and the loess contain $CaCO_3$ in considerable quantities. As a result of weathering during soil genesis the ground-water flowing towards the lakes will exsolve from the aforementioned sediments those components, i.a. Ca^{++} and Mg^{++}, and transport them into the Lakes.

The chemical composition of ground-water sampled from a few boreholes has been examined. The results are shown in Table 1. As evident from the tabulation, the ground-water in the vicinity of the lakes contains significant quantities, 700 to 4000 milligrams per litre, of dissolved salts. Of these, Ca^{++} is present in a quantity of 16 to 160 mg/l, Mg^{++} in 8 to 150 mg/l. Similarly important are Na^{+}, HCO_3^{-} and H_2SiO_3 and in some cases CO_3^{--} as well. Thus, the ground-water flowing towards the lakes is already a water containing a considerable amount of dissolved solids.

The characteristics of the water reaching the lake develop under diversified circumstances. The Danube-Tisza Interfluve is characterized by an unevenly distributed annual rainfall of 500 to 600 mm. The mean temperature in July does not exceed 22 °C, the maximum of the July average during 50 years in turn is not higher than 25 °C. Sometimes, a high temperature is coupled with droughts keeping on for several weeks. The water body of the Fülöpháza lakes is scarcely a couple of decimetres thick, so their surface area is disproportionately large compared to their volume of water, hence the intensive evaporation in the lakes. The waters are markedly alkaline, their pH in summer being above 9, often reaching even 10, moreover 11, in value.

The fluctuation of lake-water temperature is considerable even within considerably short spans of time, viz. diurnally. Naturally, under such circumstances large-scale chemical changes from season to season, or even diurnally, can be observed in the waters, both in respect of the quantity of the dissolved salts and the ionic balance equation in them.

Nevertheless, a general feature typical of the waters is their high dissolved solids content. Water samples recovered from Lake Szappanosszék simultaneously with the sampling of boreholes, in July 1972, were analyzed (Table 1). It can be seen from the results that the total dissolved solids content of the water of the lake is higher than 15 thousand mg/l. According to Zs. DVIHALLY [1970] and J. SZÉPFALUSI [1970], however, it can exceed even 25 thousand mg/l in exceptional cases.

Most of the Interfluve lakes, including those of Fülöpháza, will lose their natron nature in winter, when they contain carbonates and their pH value and al-

kalinity will considerably decrease, too. In winter time the decline of assimilation by plants and the predominance of dissimilation as well as the contribution of autumn and winter precipitations lead to an accumulation of CO_2 in such a high quantity in the water that the rate of $CaCO_3$ precipitation is gradually diminished, as $CaCO_3$ is transformed into calcium hydrocarbonate according to the following reaction equation:

$$CaCO_2 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2.$$

Because of the increase of free CO_2 during winter the Ca^{++} getting into the lake and deriving from the ground-water will remain in the form of solution and a part of the carbonate silt deposited earlier on the bottom of the lake will be dissolved so that the quantity of Ca^{++} can increase to tenfold the summer time figure. Whereas in summer the carbonate and hydrocarbonate content of most of the water is quasi equivalent to the quantity of Na^{++}, in winter a considerable part of Ca^{++} is fixed to Ca^{++}. In spring time the quantity of assimilating organisms will increase again. So first the free and then the equilibrial CO_2 is consumed and the chemical equilibrium established in winter will be upset. Under the effect of warming up, the evaporation of water increases, provoking an increase of the concentration of dissolved salts including Ca^{++} and Mg^{++}, though the value of the solubility product of Ca^{++} and Mg^{++} does not increase proportionately. This process will reduce the solubility of CO_2 as well. With the reduction of CO_2 and the increase of pH, $CaCO_3$ and $CaMg(CO_3)_2$ will gradually precipitate from lake water and thus the Ca^{++} and Mg^{++} content of the water will decrease. After the total loss of free and equilibrial CO_2 the plants making photosynthesis will consume the half-fixed CO_2 reserves of $NaHCO_3$, so calcium carbonate will precipitate from the lake water and gradually increase in it, while the Ca^{++} and Mg^{++} content will decrease and the pH and alkalinity value increase. In summer, on account of the increasing light conditions, the intensity of light is so high that dissimilation gets predominant as soon as the optimum is exceeded. In such cases, the entire process will set in inversely.

According to investigations by P. KRIVÁN [1953], the character of the chemical processes taking place in the lakes is influenced, beside the foregoing, by other physical (reduction of pressure and wave action) and chemical factors, such as the actual morphological position of the lakes, as well.

Precipitation of carbonate silt in an alkaline environment is indicated by the poverty of the gastropodal fauna represented, in a low number of specimens, by some species comparatively insensitive to alkalinity [A. HORVÁTH, 1950; M. MUCSI, 1963; A. RICHNOVSZKY, 1970].

The geological result of this phenomenon consists in the fact that Ca^{++} and Mg^{++} introduced every year into the lake will repeatedly precipitate as $CaCO_3$ and $CaMg(CO_3)_2$ and then settle as a layer of carbonate silt on the bottom of the lake.

As shown in the foregoing, the carbonate silt bed of Fülöpháza can be subdivided, on the basis of origin and composition, into three parts.

According to M. M.-FARAGÓ [1966, 1969], the middle member containing the highest percentage of carbonate was deposited at the end of the dry hazelnut stage of the Holocene and the first half of the oak stage.

The upper part less rich in carbonate, but richer in clay was accumulated in the subsequent period, *i.e.* from the second half of the oak stage to the present-day beech stage. The lower carbonate and higher clay content of the latter is accounted for by the relatively higher humidity of the present-day climate compared to that of the oak stage. Notably, compared to the hazelnut and oak stages, a lower amount

of carbonate can precipitate under present-day climate. The lower part of the carbonate silt precipitated from downward-migrating waters after the time of deposition of the two members overlying it.

It is interesting that the dolomite fraction of the carbonate silt is brought about partly as a result of syndiagenetic precipitation of a synsedimentary deposit. Deposits of similar type are known to occur in alkaline seas of high salt concentration and natroncontaining lakes of deserts. This genetic mechanism of dolomite was dealt with in detail by H. E. USDOWSKI [1967, 1968]. According to his results, the transformation of calcium carbonate into dolomite may be enhanced or even provoked by the syngenetic substitution of Mg^{++} for Ca^{++}. This is the so-called early diagenetic dolomitization that can even be increased by the exposure of still not completely consolidated sediments to subaerial conditions. At the Fülöpháza lakes, on account of the dessication of the lakes, carbonate silt often happens to be exposed to daylight. Accordingly, in some cases, this also can provoke some dolomitization.

A considerable part of the carbonate silt has been buried by wind-blown sand of Holocene origin. Owing to burial, the area of the lakes varied at a swift rate. For this reason, the extension of the carbonate silt does never reflect the one-time extent of the lake, but other changing development.

Because of the evaporation of the capillarilylifted, saline ground-water in deeper patches in the neighbourhood of the lakes and of the waning surface water of the lakes, it is mainly $NaHCO_3$ and Na_2CO_3 soluble in water that are concentrated and precipitated. In these places calcareous, sodaic soils of solontchak-solonets type are formed. At renewed rainfall a part of the soda, often segregating even at the surface, is washed by rainwater into the lake, thus increasing its alkalinity.

This is how the precipitation of lime, dolomite and natron soda brings about that peculiar geological environment in the vicinity of Fülöpháza, Danube-Tisza Interfluve, whose peculiar present-day appearance as well as its Holocene history are good and sound reasons and arguments accounting for the conservation of the area and for its inclusion in the Kiskunság National Park.

CONCLUSION

1. The neighbourhood of the natron lakes of Fülöpháza, Kiskunság, National Park, Hungary, is a wind-blown sand area. The lakes were formed in early Holocene time in depressions between ranges of wind-blown sand of NW—SE orientation brought about by predominant winds. Their base is made up of latest Pleistocene loess or earliest Holocene wind-blown sand.

2. The area has a continental climate with a very hot summer temperature and a high frequency of droughts without any precipitation for several weeks. In this environment, on account of heavy evaporation, the dissolved salts are largely concentrated in the scarcely a couple of decimetres of lake water thickness, a process further enhanced by recharging ground-water flow.

3. Under the influence of various factors (vegetation. rapid changes in temperature, wave action, etc.) calcium carbonate and dolomite are still being precipitated even today from this lake water of high salt concentration and alkalinity.

4. In the deeper patches in the neighbourhood of the lakes, capillarily-lifted, saline groundwater will evaporate, thus leading to the formation of calcareous, sodaic soils of solontchak-solonets type. Meteoric water will introduce a part of the subaerially-segregated soda into the lakes, thereby increasing their alkalinity.

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ORGANIC AND INORGANIC HIEROGLYPHS FROM THE LATE PALEOZOIC OF SOUTHERN HUNGARY

Á. BARABÁS-STUHL

In the Late Paleozoic sequence explored by the borehole Turony-1 on the northern border of the Villány Mts in Southern Hungary *(Fig. 1)*, a great deal of sedimentary external and deformation structures were found on the bedding planes of the fine-clastic sediments. The formers originate from mechanical effects of co-eval animals or represent prints of propagating organs of plants. The letters indicate penesynsedimentary features of the bedding surfaces produced from liquefaction of the tiny sandy layers within the beds.

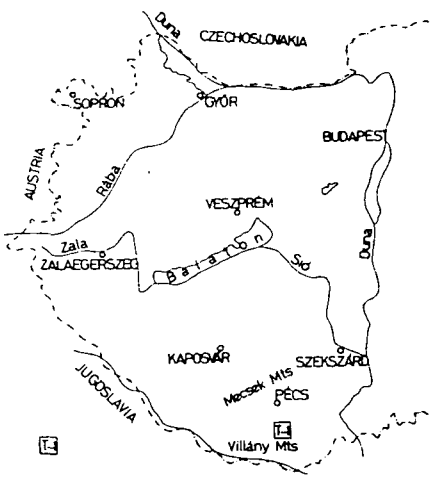


Fig. 1. Location of the borehole Turony-1.

The extension of these structures is limited, because they are visible only on drill samples. This is why both the study and the determination of them — with exception of two footprints — is only of approaching value. In spite of this their illustration can be of importance, because such structures were found in the Late Paleozoic of Hungary till now only in the mentioned place.

After crossing of the Late Neogene, Middle and Lower Trias, Late and Middle Permian, the drilling ended in Permo-Carboniferous beds *(Fig. 2)*. The bedding surface and deformation structures were found in the lower section of the borehole,

in purlish, well-bedded, sericite-bearing, finegrained sandstone and siltstone beds between 1165—1450 m. The Permocarboniferous age of this bedgroup was determined partly on the ground of the well-preserved footprints of a primitive *Amphibian,* partly with help of an ensemble of Lower Permian *Sporomorpha* coming from the coarser-grained sandstone beds that overly the formers after a smaller break of tectonical origine.

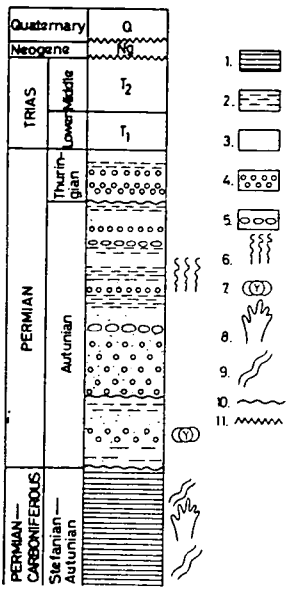


Fig. 2. Geological profile of the borehole Turony-1.
1. Alternation of fine grained slaty sandstone, siltstone and shaly mudstone. *2.* Fine and small grained sandstone. 3. Middle grained sandstone. 4. Coarse grained sandstone. *5.* Conglomerate. *6.* Traces of creeping of worms. *7.* Sporomorphs. *8.* Footprints. *9.* Inorganic hieroglyphs. *10.* Tectonical contact. *11.* Erosional unconformity.

The over-mentioned footprint determined by DR. H. HAUBOLD (University of Halle, DDR) as *Antichnium (Saurichnites) salamandroides* (GEINITZ) is stratigraphically very important (Plate I, *Fig. 1*). After studies of DR. HAUBOLD it can be found namely alone in the Stephanian and Autunian stages of the Late Paleozoic of Thuringia; but in the Saxonian stage it is already absent. So its presence of absence is significant for the separating of the Autunian and Saxonian.

An other footprint could be determined as *Platytherium psammobates* BARKAS known from the Carboniferous of the British Isles (Plate II, *Fig. 6).*

The found structures can be devided into the following groups:

EXTERNAL STRUCTURES:

I Bioglyphs

1. Footprints of primitive Amphibians
2. Prints of propagation organs of plants Sporangia of a primitive Pteridophyte Macrospores
3. Uncertain organic traces

II Mechanoglyphs

1. Current scours
   Flute moulds (?) deformed by loading
   Small longitudinal furrows
   Dendritic-ridge moulds (?)
2. Tool marks
   Broad groove mark
   Prod moulds
   Bounce moulds
   Chevron mark
3. Ripple marks

DEFORMATION STRUCTURES:

I Sand injections
1. Sand volcanoes

All these refer to an intermittently desiccated, shallow fresh-water environment controlled occasionally by rather quick currents.

EXPLANATION OF PLATES

PLATE I

1. *Antichnium (Saurichnites) salamandroides* (Geinitz 1861) Haubold 1970. Borehole Turony-1. 1220 m. *On the left:* mould; *on the right:* print.
2—3. Footprints unknown primitive *Amphibians*. Borehole Turony-1.
2. On the left: mould; *on the right:* print. 1423 m. *3. On the left:* print; *on the right:* mould. 1399 m.

PLATE II

1—5. Footprints of unknown primitive *Amphibians*. Borehole Turony-1.
1. On the left: mould; *on the right:* print, both associated with prod marks (1331 m). *2—3.* Moulds of footprints (1301 m). *4. On the left:* print; *on the right:* mould (1358 m). *5.* Very small footprints. (1301 m).
6. *Platytherium psammobates* Barkas (1301 m).

PLATE III

1—2. Sporangia of a primitive *Pteriodophyta*. Borehole Turony-1. 1450 m and 1288 m, respectively.
3. Macrospores. Borehole Turony-1. 1444 m.
4—5. Organic traces of uncertain origine. Borehole Turony-1. 1375 m and 1354 m, respectively.

PLATE IV

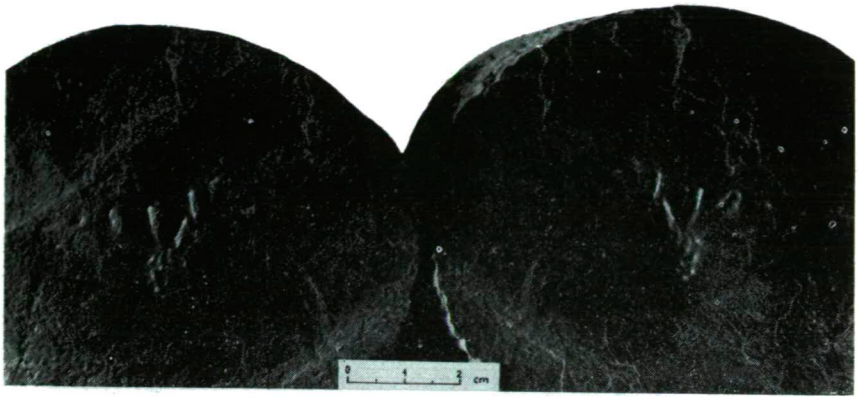
1. Organic rest of uncertain origine. Borehole Turony-1. 1352 m.
On the left: mould; *on the right:* print.
2. Ripple marks associated with prod moulds (?). Borehole Turony-1. 1347 m.
3. Flute moulds deformed by loading. Borehole Turony-1. 1370 m.
4. Small longitudinal furrows. Borehole Turony-1. 1285 m.
5. Broad groove mark. Borehole Turony-1. 1430 m.

PLATE V

1. Dendritic-ridge molds (?). Borehole Turony-1. 1349 m.
2. Prod moulds. Borehole Turony-1. 1438 m.
3. Prod moulds associated with small bounce marks. Borehole Turony-1. 1332 m.

PLATE VI

1—2. Chevron mark. Borehole Turony-1. 1300 m.
On the left: print; on the right: mould.
3. Small prod marks. Borehole Turony-1. 1313 m.
4. Chevron mark. Borehole Turony-1. 1349 m.
5. Sand volcanoes. Borehole Turony-1. 1416 m.



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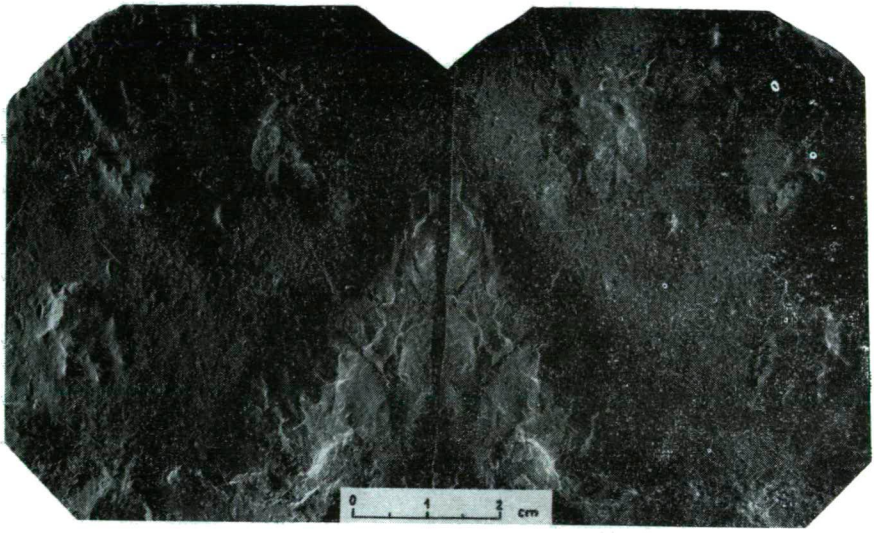

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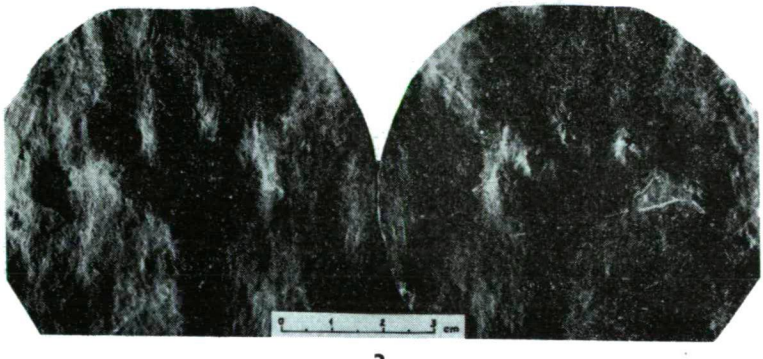

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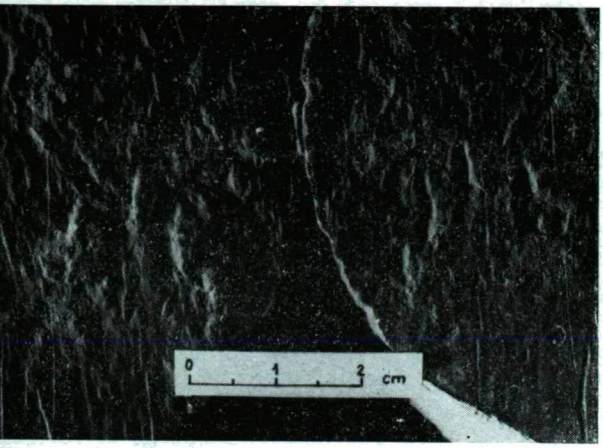

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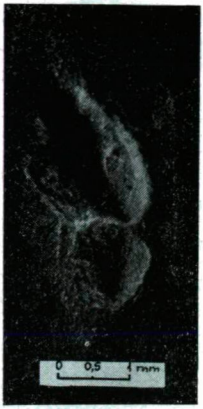

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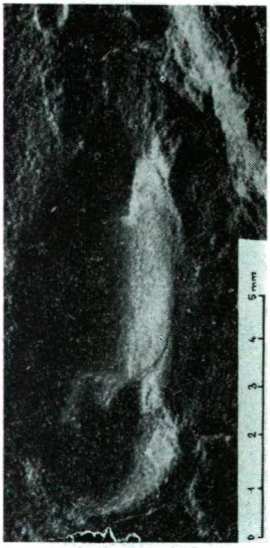

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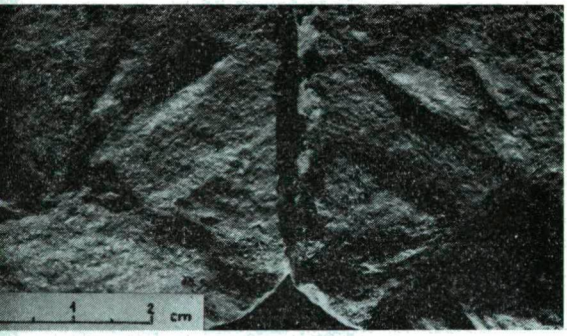

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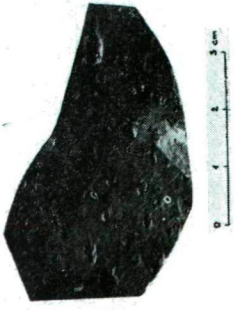

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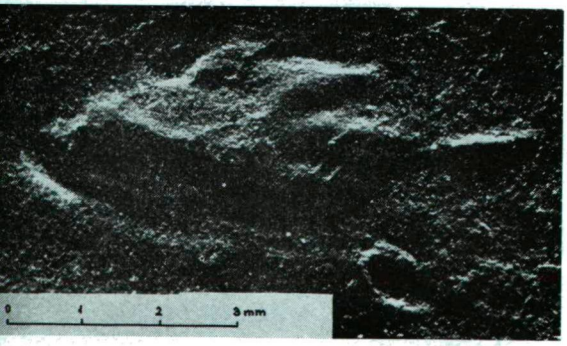

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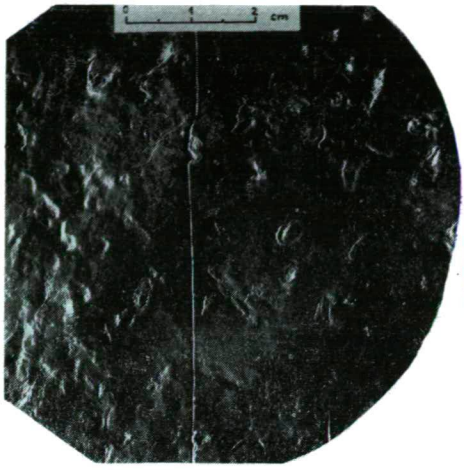

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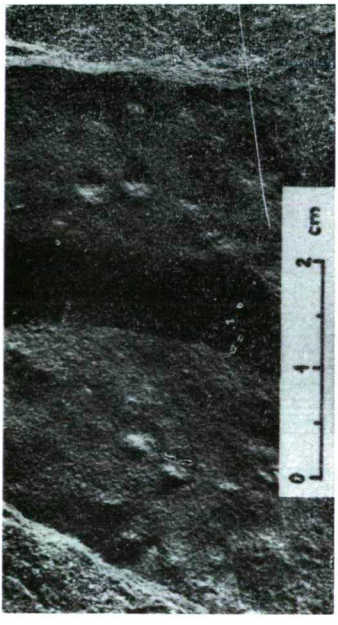

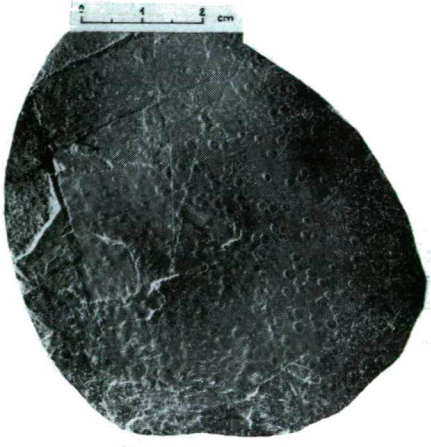

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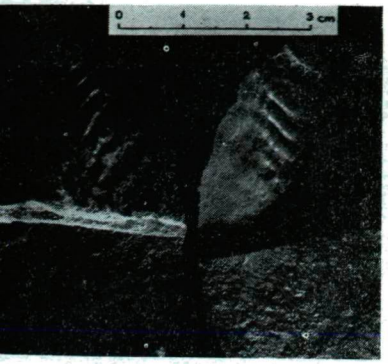

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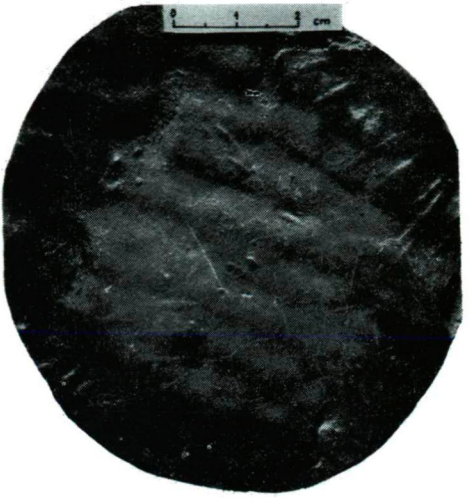

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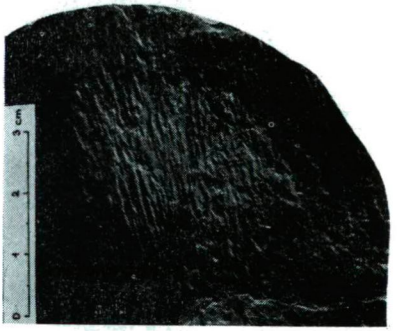

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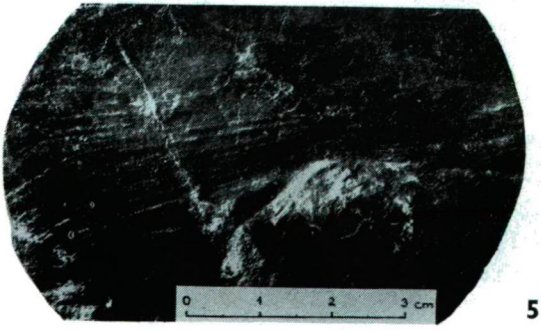

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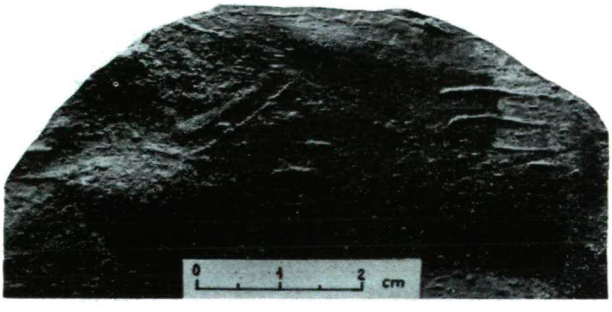

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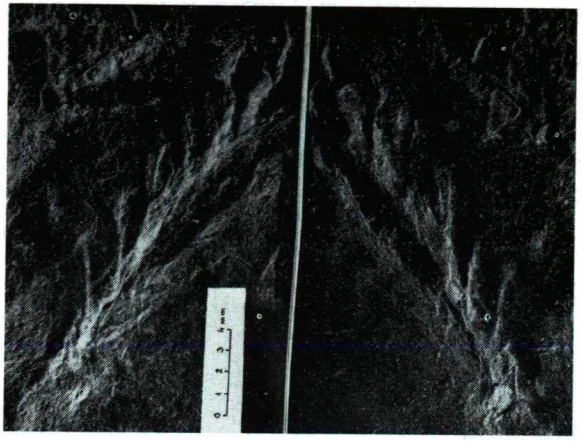

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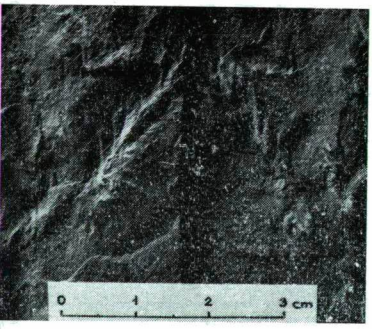

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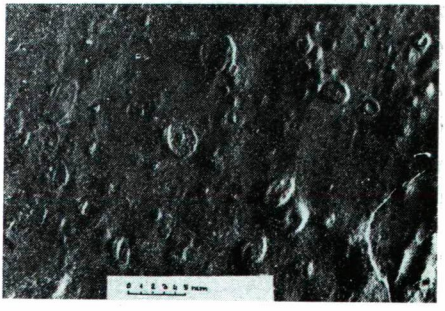

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A COMPARATIVE PETROLOGIC STUDY OF SARMATIAN PYROXENE-ANDESITES NEAR TELKIBÁNYA—PÁNYOK (TOKAJ-MTS, NE-HUNGARY)

M. NÉMETH

ABSTRACT

As a result of the author's investigations, it has been stated, that the acidic pyroxene-andesite of the belt between Szurokhegy in Kéked and Magostér in Telkibánya (both in NE-Hungary) belongs to the leucogabbroidic type of igneous rocks defined by NIGGLI. (The foliated rocks of the Hosszúkő in Telkibánya characterized by parallel lamellae belong to this group, too.) This fact refers to the basic character of the original magma corroborated also by the presence of hypersthene and bronzite as well as that of diopside and endiopside from among the monoclinic pyroxenes. The latter minerals are missing in the foliated andesite of Hosszúkő. This can be explained by a relatively rapid ascendence of the rock as compared to that of the acidic pyroxene-andesite. In this case there was not time for a fractional crystallization.

The path of the acidic pyroxene-andesite interrupted by "stopovers" (i.e. by magma-chambers) could be traced easily by minerals which crystallized from it. From the clinopyroxene lamellae of the hypersthene appearing first and containing 51—52 mol% of $MgSiO_3$, Ca^{2+} and Fe^{2+} ions have been removed in a temperature range of 800—1000 °C. This phenomenon — together with an intake of OH^- ions — have resulted in uralitization consisting of structural realignment and starting along transversal clefts. (The clinohypersthene lamellae are lamellae parallel to the (100) plane of the orthopyroxene with higher Ca^{2+} and Fe^{2+} content as compared to their environment.) Assuming that more significant Si addition from the surroundings necessary for pyroxene → amphibole transformation is impossible, Mg^{2+} and Fe^{2+} are released by this transformation process. The release of Mg^{2+} has lead to formation of $MgSiO_3$-rich orthopyroxene types (i.e. bronzite), while the released Fe^{2+} content which attained a higher oxydation-reduction potential in an OH^--rich environment, could not be fixed in the orthopyroxene, but have been separated as hematite. Thus the bronzite-formation is promoted by the amphibolization in a double way.

In this environment characterized by relative low Fe^{2+} content, diopside and endiopside are formed instead of augite. Lacking this quiet, fractional crystallization clinohypersthene and augite have formed in the foliated andesite.

Under thicker cover and in presence of higher volatile concentration even the chloritization of the uralite has started (Hasdát-völgy), and the released Ca content has been fixed in apatite crystals. This phenomenon is the sign of a commencing propylitization, though in that case higher temperature (epidote) and H_2S addition (pyrite) should also be reckoned with.

INTRODUCTION

This study deals with the ortho-rocks of the so called "acidic pyroxene-andesite" and "foliated pyroxene-andesite" sequence of Sarmatian age in the area between Telkibánya—Pányok *(Fig. 1)*. The ortho-andesite is represented by samples of acidic pyroxene-andesite from the Nagy-hegy near Pányok, from the quarry of Pányok, from a pasturage in front of the inlet of the Hasdát-völgy, as well as from the Baglyas-völgy in Telkibánya. These are compared according to the mineralogical and petrological composition to the foliated orthoandesite from Hosszúkő in Telkibánya representing a younger magmatic phase.

The author's aim was a more detailed mineralogical investigation of the pyroxenes in the acidic- and foliated pyroxene-andesites; the determination of the crystal-

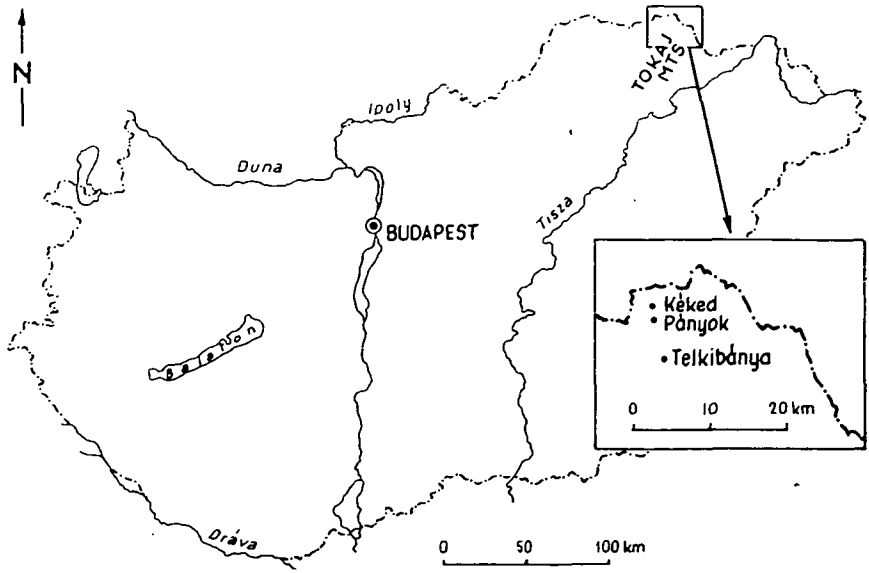

Fig. 1. Location of the investigated area.

lization sequence of the pyroxenes as well as observations concerning the alterations of pyroxenes.

In the course of microscopic investigations the composition of the orthorhombic and monoclinic pyroxenes in mol% has been determined by universal stage method. In the case of orthorhombic and non-twinned monoclinic pyroxenes only the 2V has been measured, while for monoclinic crystals twinned by (100) plane values of 2V, γ/c, A/c have been estimated. Substituting the data collected this way into the so-called Hess-diagram the composition of pyroxenes in mol% can be stated [KUBOVICS, 1968; SZTRÓKAY, K. *et al.* 1970].

The mineralogical composition in volume percents and grain-size distribution have been measured along straight lines (8 lines for each thin section).

COMPARATIVE STUDY OF THE PYROXENE-ANDESITES

Petrologic description

1. According to the microscopic observations the *acidic pyroxene-andesite* is composed not only of orthominerals. Uralitized-chloritized pyroxenes and opacitic amphiboles also can be found always. The quantity of these, however, is under 5%, thus the rock involved is allowed to be defined as ortho-andesite.

As for the phenocrysts of the ortho-andesite, the *plagioclase* crystals are platy and twinned, mostly by Carlsbad-law. In general, three generations could be separated:

1) Plagioclases with a length of 3000—500 μ.
2) Plagioclases with a length of 500—180 μ.
3) Plagioclase lathes of the groundmass.

The plagioclase generations listed above differ from each other mostly in their inclusion content. The plagioclase crystals of the first generation have groundmass-inclusions either forming zones or spacing parallel to the longitudinal axis of the crystals. In the sample taken from the entrance of the Hasdát-völgy, sporadically first generation plagioclase crystals with clinopyroxene inclusions can be found (Plate II. *Fig. 1*).

So-called "plagioclase-knots" occur also frequently. These are composed of well rounded (i.e. resorbed), sometimes sericitic first-generation plagioclase grains and hypersthene crystals with a number of longitudinal clefts and altered along transversal cleavages (Plate I, *Figs. 1—2*). Every now and then one or wto clino-pyroxene grains could also belong to such an holocrystalline nodule. The plagioclase crystals of the second generation are inclusion-free, unaltered and angular. Their composition is of labradorite-andesine character with an 50% of anorthite content in general.

Mafic components of the rock are mostly orthorhombic pyroxenes, clinopyroxenes as well as amphiboles. Their sizes remain under those of the plagioclase crystals. The *orthopyroxenes* are the most abundant mafic components having two generations of different composition. The first one is characterized by larger, elongated crystals (1000—500 μ in length) of fairly platy appearence. The average of the 2V values is −55,2° varying between −51 to −57,5° (Table 1). This average value means an orthorhombic pyroxene with an $MgSiO_3$ content of 51—52%, which corresponds to the composition of the *hypersthene*. These pyroxene crystals are characterized by the dominance of the longitudinal cleavages as well as by frequent occurrence of magnetite inclusions with a diameter of 30—100 μ (Plate I, *Figs. 3—4*).

TABLE 1

2V values of orthopyroxene crystals from the Nagy-hegy in Pányok

First generation without pigeonite-rim	Second generation with pigeonite-rim	
	Central part	Marginal part
−51°	−61°	−76°
*−52°	−61,5°	−77°
−55°	−62°	−82°
−56,5°	−67°	−83°
−56,5°	−68°	−83°
−56,5°	−69°	
−57°		
−57,5°		
Average −55,2°	−64,7°	−80,2°

* Orthorhombic pyroxene belonging to a plagioclase-knot.

The second generation are of shorter and less wide pyroxene crystals showing definitely lathy forms sometimes, and characterized by transversal clefts (Plate II, *Figs. 2—3*). The magnetite inclusions are much less frequent as compared those in the first generation. The average 2V value of the second-generation orthopyroxenes is −64,7° varying from −61° to −69°. As for their chemical composition, their $MgSiO_3$ content amounting to 70 mol% marks the *bronzitehypersthene* border. An emphasized increase of the 2V values could be stated in these orthopyroxene

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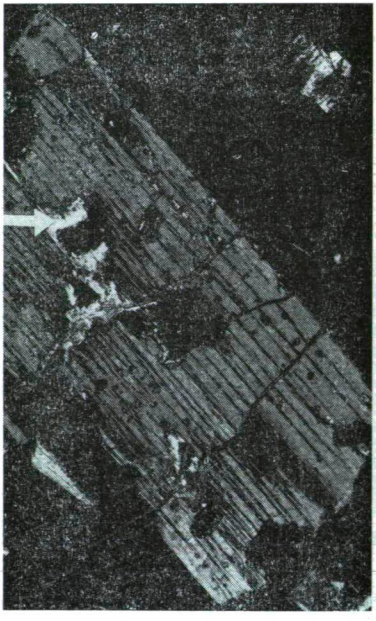

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varieties moving towards the rims, as a result of which the average value of 2V might be as high as $-80{,}2°$ (Table 1). This value corresponds to an $FeSiO_3$ content of 16—17% only, on the basis of which the minerals involved could be defined as *bronzite*. Second-generation orthorhombic pyroxenes could be repeatedly observed to have monoclinal pyroxene rims (Plate II, *Fig. 4*).

Consequently, the optically oriented coalesce of monoclinic pyroxene and hypersthene mentioned several times by earlier papers too [LIFFA, A. 1953; HERRMANN, M. 1952; SZÉKY-FUX, V. 1970 is only for the bronzitic hypersthenes of the second generation in the area involved.

The alteration processes of all orthopyroxene varieties start along transversal cleavages and advancing step by step, extend to the longitudinal cleavages too. The alteration product is a fibrous, slightly pleochroic *uralite* with length-fast elongation and showing polarization colour of first-order orange to second-order blue (Plate I, *Figs. 3—4*). The fibres are spaced parallel to the "c" axis of the orthopyroxene. The alteration process is more advanced in the case of hypersthenes of the first generation. In the andesite at the inlet of the Hasdát-völgy the weathering of the hypersthene is even more advanced. Pale green, slightly pleochroic *chlorite* and *uralite* — both after hypersthene — are frequent. In these pseudomorphoses unaltered orthopyroxene fragments are "floating" (Plate III, *Fig. 1*). Sometimes *apatite* lathes are found in the chlorite-knots. A type of chlorites with a polarization colour of first-order gray as well as lower in refractivity and less in size than the uralite fibres could be found in the uralite pseudomorphoses and along the late transversal clefts of the hypersthene; i.e. at the starting points of the alteration processes. The hypersthene crystals from the Baglyas-völgy have suffered a nontronitic alteration.

The *monoclinic pyroxenes* less in size and quantity then the orthorhombic ones, have two modifications. One of them appears to be a rim of the second generation of the orthopyroxenes mentioned above (Plate II, *Fig. 4*). These are elongated *pigeonite* crystals with 2V values of 5—8°. The other modification is made up from independent isometric crystals having octogonal sections parallel to the (001) plane. Sometimes twinning by the (100) plane can be observed (Plate III, *Fig. 2*). On the basis of their 2 V, γ/c and A/c values, these independent monoclinic pyroxenes are *diopsidic* or *endiopsidic* composition or mark the diopside→endiopside transition *(Fig. 2)*. According to DEER, W. A.—HOWIE, R. A.—ZUSSMANN, J. [1963] such joint occurrence of Ca-rich and Ca-poor phases refers to an period of quiescence, and — according to PANTÓ, G. [1964] — shows a magma chamber below a depth of 10 km [in PANTÓ, GY. 1970. p. 200]. Moreover, DEER, W. A. *et al.* [1963] stated also, that could be found mostly in well differentiated rocks jammed under the surface.

Besides the feldspar-knots already mentioned in discussing the other autigenic inclusion-type of the rocks, the monoclinic pyroxenes are dominating together with plagioclase and more rarely also with uralitized hypersthene and magnetite. The distribution of the minerals in the authigenic inclusion of the andesite of the quarry in Pányok in vol% is as follows: plagioclase 31%, monoclinic pyroxene 55%; ortho-

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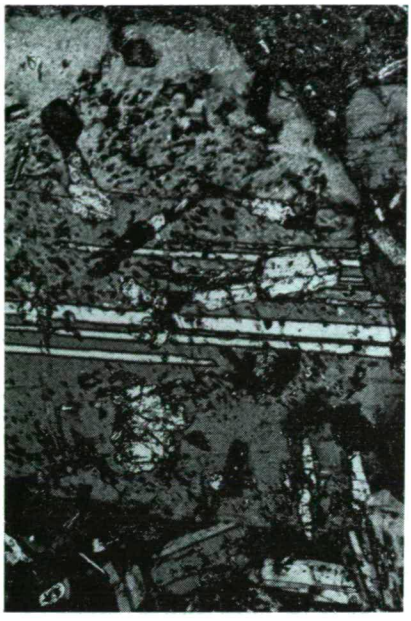
PLATE I

1. A plagioclase-knot with altered pyroxenes. — Acidic pyroxene-andesite, Pányok, Nagy-hegy— 1 N, 30x.
2. The same. — 2 N, 30x.
3. An uralitized (arrow) orthopyroxene (hypersthene) of first generation with magnetite inclusion. — Acidic pyroxene-andesite, Pányok, Nagy-hegy — 1 N, 72x.
4. The same. — 2 N, 72x.



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pyroxene 11%, opague minerals 3%. These "mineral nodules" are of holocrystalline character. Their grain-size cumulative curve is shown in the *Fig. 3.* In and around the holocrystalline nodules of the sample from Hasdát-völgy, chloritized biotites, strongly pleochroic in their unaltered parts, have an widespread occurrence (Plate III, *Fig. 3*).

The *amphiboles* are of 2000—600 μ in length, and are coated by thicker-thinner opacitic rim, while their central part is composed of clay minerals. Small plagioclase inclusions up to 50×40 μ, and — rarely — hypersthene could be found in it. Moreover in the amphibole from the Hasdát-völgy, biotite inclusions also could be observed. There are more amphiboles than pyroxenes in the sample from Baglyas-völgy, but it may be the result of hypomagmatic effects.

The *groundmass* of the rock is composed of microlits of acidic plagioclase and clinopyroxenes as well as magnetite grains. Its texture is microholocrystalline porphyritic. The grain-size cumulative curve of the samples from Nagy-hegy in Pányok has not any distinct maximum and shows an even running. The other samples, however, are characterized by steep curves showing only one maximum *(Fig. 4).* The latter type of curves refers definitely to a subvolcanic solidification as opposed to the textural character of the Nagy-hegy in Pányok forming a transition between the subvolcanic and surficial solidification.

The microlits of the groundmass of the andesite from the quarry in Pányok are of 5 μ in size, while their lower limit is 10 μ in the samples taken from the Hasdát-völgy. The accessorial components of the rock are: *magnetite, limonite, hematite* and — in the sample from the Hasdát-völgy only — even corroded *quartz* grains can be seen. The quantitative composition of the acidic pyroxene-andesite is given in vol. percents in the Table 2.

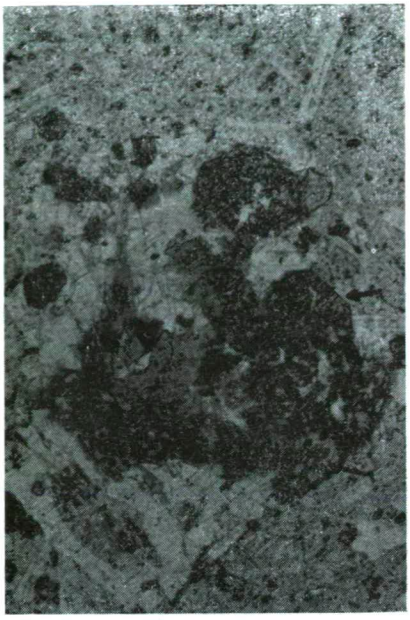
TABLE 2

The mineralogical composition of the acidic pyroxene — andesites in vol. percents

	Acidic pyroxene—andesite of Pányok			Foliated pyroxene-andesite of Telki-bánya
	Nagy-hegy	Quarry	Hasdát-völgy	Hosszúkő
Groundmass	25	13	25	56
Plagioclase	57	70	63	32
Orthopyroxene	11	11	6	7
Clinopyroxene	3	4	4	4
Opacitic amphibole	2	1	1	—
Opaque	1	0,5	0,5	1
Other minerals	1	0,5	0,5	—
Total	100	100	100	100

PLATE II

1. A plagioclase with pyroxene inclusion. — Acidic pyroxene-andesite, Pányok, Hasdát-völgy. — 2 N, 72x.
2. An orthopyroxene of second generation formed shape of a lath. — Acidic pyroxene-andesite, Pányok, quarry. — 2 N, 53x.
3. An orthopyroxene of second generation. — Acidic pyroxene-andesite, Pányok, Nagy-hegy. — 1 N, 72x.
4. An orthopyroxene of second generation with pigeonite-rim (arrows). — Acidic pyroxene-andesite, Pányok, Nagy-hegy. — 2 N, 120x.



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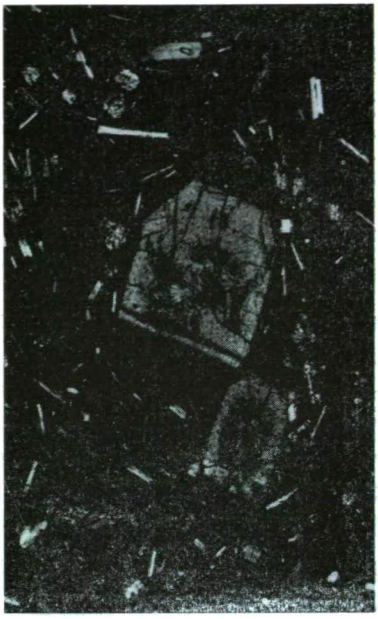

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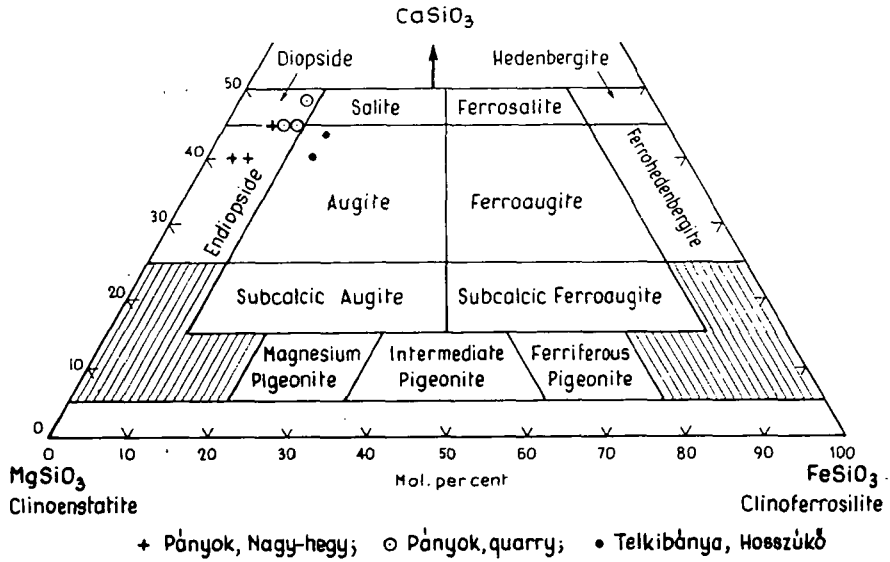

Fig. 2. The investigated clinopyroxenes in the system by POLDERVART—HESS [1951].

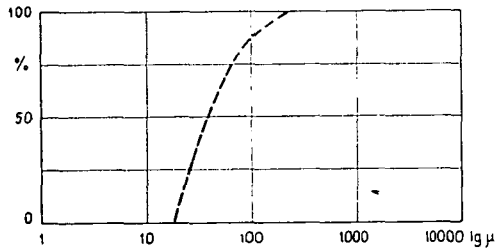

Fig. 3. Grain-size cumulative curve of pyroxene-knot occurred in acidic pyroxene-andesite. — Pányok, Nagy-hegy.

2. The chemical composition of the *foliated pyroxene-andesite* of Hosszúkő in Telkibánya is similar to that of the acidic pyroxene-andesite excepting the quantity of the alkalies in which slight differences can be stated. According to the geologists having mapped this area, the formation of these foliated rocks has taken place at the end of the Sarmatian [M-34 XXXIV Sátoraljaújhely, 1966]. Along the lamellae of this rock mineral assemblages of low-temperature hydrothermal origin have been

PLATE III

1. Pseudomorphous uralite, chlorite after hypersthene in a plagioclase-knot with unaltered pyroxene-particles (arrows). — Acidic pyroxene-andesite, Pányok, Hasdát-völgy. — 1 N, 53x.
2. Twins of clinopyroxenes. — Acidic pyroxene-andesite, Pányok, quarry. — 2 N, 72x.
3. A holocrystalline nodule of plagioclase, chloritized hypersthene, biotite, chlorite. — Acidic pyroxene-andesie, Pányok, Hasdát-völgy — 1 N, 72x.
4. An inclusion derived from basement rocks. — Acidic pyroxene-andesite, Pányok, quarry. — 2 N, 30x.

found. These assemblages consisting of small prisms of *barite* with a lot of *calcite* needles and *strontianites* on it have not been known until now. The strontianite gives a whitish transparent and fibrous mineral aggregate upon the surface of the minerals formed earlier.

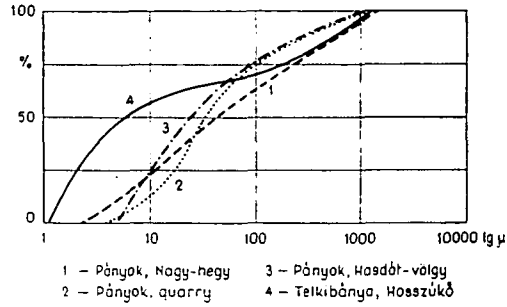

Fig. 4. Grain-size cumulative curves of acidic pyroxene-andesite (1—3) and that of foliated pyroxene-andesite (4).

The *plagioclase* crystals of the rock are not zoned, are not altered and do not contain any glass or opaque inclusions. There are two plagioclase generations:

1) a generation consisting of elongated crystals of 1200—100 μ;
2) the plagioclase lathes of the groundmass.

The mafic components are: hypersthene and monoclinic pyroxenes. The amphiboles are lacking. The *hypersthene* is of elongated, lathy appearance showing slight pleochroism (yellowish and greenish) and an oblique extinction of 5—10° as compared to the direction of the elongation. The average of the 2V values is −60° (with −57° and −65° as extreme values); i.e. the hypersthene crystals contain 64 mol% of $MgSiO_3$. The monoclinic pyroxenes are of augitic composition showing twins by (100) frequently *(Fig. 2)*.

The authigenic inclusions made up from pyroxene and plagioclase can be found in this rock too. The other type of the monoclinal pyroxenes, the *pigeonite,* however, occurs in this rock only as rim of some hypersthene crystals. All the pyroxene grains are absolutely unaltered. There are shapeless and resorbed feldspar and pyroxene debris of size comparable to that of the phenocrysts scattered all over the rock.

The characterictic accessorial component of the rock is the *magnetite.*

The fissures of the sample is filled by fibrous, radial, slightly pleochroic *barite,* being length-fast in the direction of the elongation, showing a polarization colour of first-order yellowish gray, and characterized by straight extinction. The lower limit of the sizes of the microlites in the *groundmass* is around 1 μ. The texture of the rock is microholocrystalline-porphyritic. Its grain-size cumulative curve shows two maxima *(Fig. 4)*. Grains of the 100—10 μ are almost totally missing, and the curve refers to a solidification of the surface. The redissolved mineral debris might point to a "stopover" of the ascending magma. After this interruption the eruption has taken place within a relatively short period. Supposedly there may have been an other but less significant disturbing factor on the way of the ascending magma as it is testified by the presence of the pigeonite in the authigenic pyroxene inclusions. Consequently the eruption of the foliated pyroxene-andesite at the end of the Sarma-

tian has taken place more smoothly than that of the acidic pyroxene-andesite. As a result of this relative smooth eruption, preconditions necessary for forming uralite have not existed, and the orthopyroxenes which have crystallized belong to the hypersthene-group.

In connection with the ortho-pyroxene-andesites, the *basement rock inclusion* found in the rock of the quarry of Pányok is also to be mentioned. (Plate III, *Fig. 4.*). Its size is 6×2,5 mm, and its components are: quartz (30—120 μ), magnetite (30—250 μ), biotite (200—370 μ). The biotite plays a more significant role in the central part of the inclusion. The distribution of the hematite shows a pattern parallel to the longitudinal axis of the inclusion.This phenomenon undoubtedly refers to the partial melting and redistribution of the material of the inclusion. A contact zone consisting of epidote crystals can be observed in the andesite aruond the inclusion. The andesite is holocrystalline in a 180—560 μ wide zone around the inclusion. Over this zone the feldspar lathes of the groundmass are more and less parallel to the outlines of the inclusion. Similar basement inclusions are described by SZABÓ, J. [1867] from Szokolya in Erdőbénye, and from Párkány in Tállya; and by SZÁDECZKY GY. [1897] from Rudabányácska and Kovácsvágás, as well as by HERRMANN, M. [1952] in the andesite from Borinzás.

On the basis of the petrologic characteristics listed above, the ortho-andesites described here could be qualified as monoclinic pyroxene bearing hypersthene-andesite. The only exception is the sample from Baglyas-völgy, which — in turn — could be pigeon-holed to the group of the amphibole bearing hypersthene-andesites.

The term "monoclinic pyroxene bearing" is considered more appropriate as opposed to the term "augitic" used so far, as the monoclinic pyroxenes in the acidic pyroxene-andesite of the area have been determined as diopside and endiopside. The attention had already been directed by HERRMANN, M. [1952] and by LIFFA, A. [1953] to the diopsidic character. The author's investigations, carried out by universal stage method, have confirmed this fact allowing the exact determination of the composition of the minerals.

CHEMICAL CHARACTERISTICS

According to VINOGRADOV [1955] the average SiO_2-content of the andesite is 57,00%. The acidic pyroxene-andesites in the Tokaj Mts., however, have an SiO_2 content as high as 60,01 % in average [M-34 XXXIV. Sátoraljaújhely, 1966] (Table 3).

The question arose, whether the term "andesite" is correct, in our case? Whereas the classical term "andesite" has been defined by our predecessors taking into consideration the phenocrysts of the rock only (i.e. neglecting the chemical and mineralogical composition of the groundmass), the acidic pyroxene-andesite can be rightly considered as andesite in this respect. SZÁDECZKY—KARDOSS, E. remarked [1968, p. 149], that the classification based on mineral components estimated from the chemical composition of the rock by a theoretical way, came to a deadlock, if this important character of the ancient nomenclature had not been taken into consideration, because the majority of the andesites got to the rhyodacite-field of the RITTMANN-diagram on the basis of their estimated minerals [GYARMATI, P. 1961]. This is the case, because in the course of a total crystallization an other mineralogical composition is formed, as, though with progressing of the crystallization more and more acid minerals, even quartz ,originated from the more and more acidic melt, the fields of the diagram have been determined on the basis of the classical definition. The difficulty of the andesite problem is underlined by the fact that famous foreign petrologists [e.g. AHRENS, L. H., 1964], studying the chemical composition of the igneous rocks by statistical methods, have neglected the andesite and diorite, stating that the SiO_2 distribution of these two rock-types is rather complicated without reason, and admittig that these names mark a rather large group of rocks instead of well defined rocks with fairly constant composition.

TABLE 3

Chemical composition of the Sarmatian pyroxene-andesites compared with international average of andesites by VINOGRADOV *[1955]*

	International average	Acidic pyroxene-andesite					Foliated pyroxene-andesite
		Average for the whole Tokaj Mts*	Kéked, Szurok-hegy	Pányok, quarry	Telkibánya, Magostér	Pányok, Nagy-hegy	Telkibánya, Hosszúkő
Analyst:	—	—	Emszt, K.	Ikrényi, K.	Emszt, K.	Ikrényi, K.	Ikrényi, K.
	%	%	%	%	%	%	%
SiO_2	57,00	60,01	57,38	60,00	60,03	62,40	61,30
TiO_2	0,79	0,55	1,10	0,65	0,86	0,80	0,80
Al_2O_3	17,50	17,22	16,44	16,65	16,72	15,95	16,50
Fe_2O_3	3,72	2,43	1,66	2,11	3,01	2,34	1,07
FeO	3,31	3,07	4,22	2,96	3,26	2,75	3,99
MnO	0,17	0,11	0,12	0,07	0,07	0,07	0,09
MgO	3,64	3,55	5,04	4,40	4,30	3,90	3,70
CaO	6,70	6,68	7,70	7,60	5,64	6,40	7,30
Na_2O	3,62	2,40	2,68	2,52	2,36	2,28	1,96
K_2O	2,01	1,89	1,08	1,68	1,82	1,83	2,09
H_2O^-	0,83	0,81	0,28	1,18	0,57	1,16	1,06
H_2O^+		1,28	1,29		0,91		
P_2O_5	0,25	0,16	—	0,10	0,10	0,10	0,13
CO_2	—	0,03	0,16	0,20	0,17	0,09	0,20
Total	99,54	100,19	99,15	100,12	99,82	100,07	100,19

* Corrected data get from the explanations to the geologic map "M-34-XXXIV. Sátoraljaújhely, 1966".

As this question is to be solved recently too, the chemism of the rocks is compared to the VINOGRADOV's average (Table 3) remarking, that the higher SiO_2 content of our rocks is not in contradiciton to the andesite character (i.e. taking the classical definitions into consideration until a new, more exact system would not be developed). The author is of the opinion, that even the rhyodacite and dacite categories (SiO_2-content is 65—69% and 60—65% respectively) could not show any solution to this problem to be solved possibly by comprehensive statistical investigations only.

The SiO_2-content of 60,01 % does not involve an increase of the alcalies and a decrease of the CaO-content. Moreover the latter showed a slight increase in some rocks while the alkali content mostly decreased as compared to the VINOGRADOV-average. The MgO content is also higher than the international average. This phenomenon is in accordance with the more basic character of the original magma. Estimating the NIGGLI's *si-al-alc-fm-c* values and plotting them in the differentiation diagram *(Fig. 5)*, it can be stated, that parallel to the increase of the *si*-volume there is a slight and interrupted increase of *the alc* and *al* values; while the *fm* value — inspite the extremly high value from Magostér — shows a decreasing trend. The *al* and *alc* values vary parallel to one another, while the *fm* and *c* values alternate opposite to each other. On the basis of the *si-al-alc-c-fm-k-mg* values (Table 4) the rocks involved belong to the NIGGLI's leucogabbroidic type of magma.

TABLE 4

Si, al, fm, c, alk, k, mg and Q, L, M values by NIGGLI *of the Sarmatian pyroxene-andesites*

	si	*al*	*fm*	*c*	*alk*	*k*	*mg*	*Q*	*L*	*M*
Acidic pyroxene-andesite Kéked, Szurokhegy	171,2	28,8	36,9	24,6	9,7	0,20	0,61	45,0	33,7	21,3
Acidic pyroxene-andesite Pányok, quarry	188,0	30,7	33,2	25,4	10,7	0,29	0,62	49,4	35,7	14,8
Acidic pyroxene-andesite Telkibánya, Magos-tér	195,7	32,0	37,2	19,7	11,1	0,33	0,56	48,7	33,4	17,8
Acidic pyroxene-andesite Pányok, Nagy-hegy	212,0	31,9	33,5	23,3	11,3	0,35	0,58	52,0	32,2	15,8
Foliated pyroxene-andesite Telkibánya, Hosszúkő	201,2	31,8	31,9	25,6	10,7	0,40	0,57	50,0	33,4	16,6

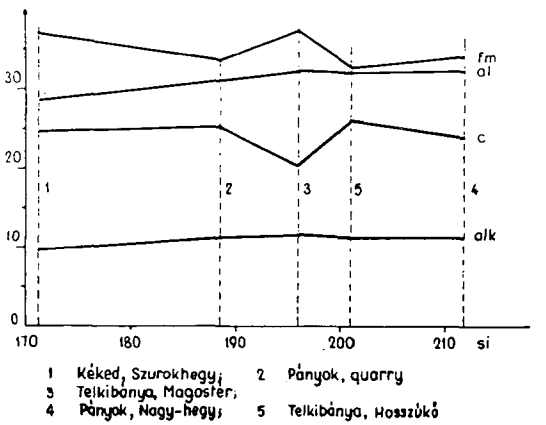

Fig. 5. The acidic pyroxene-andesite (1—4) and the foliated pyroxene-andesite (5) in the differentiational diagram by NIGGLI.

CONCLUSIONS

The first generation plagioclase crystals and larger hypersthenes, forming knots connecting to plagioclases and abundant in longitudinal clefts as well as containing $MgSiO_3$ of 51—52 mol% are considered as the first crystallized compoments of the acidic pyroxene-andesite. This hypothesis is corroborated by the very rounded, resorbed shape of the plagioclase crystals as well as by the fact that the uralitic

alteration of the hypersthene is more emphasized than that of the other pyroxenes. Similar phenomena have been described by PANTÓ, GY. [1970] from the Börzsöny Mts. (North-Hungary), stating that "by the increase of the instability of the pyroxenes the plagioclase crystals were eroded by the environmental conditions necessary for forming uralite".

According to BOLAND, J. N.—AL DUBA-EGGLETON, A. [1974] clinoenstatite is formed from orthopyroxene by lamellae more abundant in Ca^{2+} and Fe^{2+} ions than the orthopyroxene and interbedding into the latter parallel to its (100) plane. This mixed phase, however, is metastable in the temperature range of 800—1000 °C according to the experiments carried out by the authors listed above. The superflous Ca- and Fe-content of the clinoenstatite lamellae parallel to the (100) plane diffuse with a simultaneous intake of energy, while the late clinoenstatite lamellae are transformed into enstatite.

The author is forced by reasons of several types to compare the phenomenon described above to the more advanced uralitization experienced in the case of the hypersthene crystals of the first generation:

1. The orthopyroxenes of the pyroxene-andesite of Hosszúkő having a fairly uniform composition and refering to a more rapid ascending mechanism, are of clinohypersthene character and uralitization could not be observed in the rock.

2. The first generation hypersthenes of the acidic pyroxene andesites are dominated by vertical clefts being generally absent in the second generation hypersthenes. It may be therefore assumed that the vertical clefts could be correlated to the lamellae parallel to the (100) plane and more abundant in Ca and Fe. The first hypersthenes of the rock contained or contain until now lamellae more abundant in Ca and Fe and parallel to the (100) plane. During the formation of these minerals an additional ascending period of the magma may have taken place pushing the melt into an upper magma chamber with lower temperature, where the conditions were favourable even for forming amphiboles.

According to WITTELS, M. [1952] [in ILKEY-PERLAKI, E. 1961] the amphibole-pyroxene transformation could be pigeon-holed to the temperature range of 600—1000 °C, i.e. the two phases could be observed together within this temperature range. Being the clinopyroxene lamellae abundant in Ca and Fe metastable between 800—1000 °C, it should be assumed that they survived in the orthopyroxenes of quickly cooling rocks only. Though the formation conditions of the mineral involved is not given by BOLAND, J. N. *et al.* [1974] the hypersthenes of the quickly solidified andesite in Hosszúkő showing an oblique extinction of 5—10° refer to the conditions mentioned above.

Consequently in the temperature range of 800—1000 °C Ca and Fe diffusion and uralite formation should be taken into consideration as well. Thus, the alteration of orthopyroxenes could be accounted for a part of the Ca necessary for forming amphibole; naturally in addition to the Ca-quantity supplied by feldspar-resorption mentioned also by PANTÓ, GY. [1970]. Our former assumptions seem to be corroborated also by the fact, that the uralitization proceeds parallel to the longitudinal clefts of the hypersthene.

In addition to the intake of OH^-, the uralitization of the hypersthene crystals would take place by diffusion of Ca- and Fe-ions along longitudinal cleavages and by material and structural transformations at first time in the inner cavity and along transversal cleavages as well — according to the facts listed in this study so far. In contradiction to the equations described by ASKLUND [1925], STEWART [1947] [in PANTÓ, Gy. 1970] Si-addition is considered as improbable. For the orthopyroxene

$[(Mg, Fe)_2Si_2O_6] \rightarrow$ actinolite $[Ca_2(Mg, Fe)_5 Si_8 O_{22}(OH)_2]$ transformation 4 molecules of orthopyroxene would be necessary providing quantum sufficit of Si, but in this case — reckoning with OH^- addition too — an excess of $3(Mg, Fe)^{2+}$ and $2O^{2-}$ should be formed. Thus the released Fe^{2+} ion would be oxidized by an increase of the oxidation-reduction potential caused by the released O^{2-}, which, after having united with H^+, incorporated into the uralite.

On the other side, orthopyroxenes showing higher $MgSiO_3$-content than the older ones would be formed by the released Mg-ions increasing the Mg-content of the remnant melt. These orthorhombic pyroxenes, having an composition abundant in $MgSiO_3$, would be considered as the second generation marking the hypersthene-bronzite boundary. The $FeSiO_3$-content of the pyroxene would decrease, as the Fe-ions having attained a higher degree of oxidation, would be useless for forming orthopyroxenes. Thus a solution is given to the formation of first generation hypersthene of lower $MgSiO_3$ content (i.e. of lower compound-potential) prior to the formation of bronzite. The foliated pyroxene-andesite of Hosszúkő does not contain orthopyroxenes of second generation.

The Fe^{3+} content of the acidic pyroxene-andesite produced by the increased oxidation-reduction potential appears in form of hematite. The fact that the foliated pyroxene-andesite in Hosszúkő having no hematite is characterized by an Fe_2O_3: :FeO ratio of 1,07:3,99, while the same parameters in the acidic pyroxene-andesite from the Pányok-quarry and from Nagy-hegy are 2,11:2,96; 2,34:2,75 respectively, is in accordance with the author's statements .The total of the two Fe-oxides in the different rocks are almost the same.

For a comprehensive evidence of the explanation outlined above by thorough investigations elucidating even the quantitative relation between the first and second generations of the orthopyroxenes are among others to be carried out.

The formation of orthopyroxenes more abundant in Mg-ions has taken place simultaneously to the uralitization in the same magma chamber of the acidic pyroxene-andesite. With the proceeding of the uralitization their margines have become more abundant in Mg and even pigeonitization has taken place by Ca-addition. In this environment showing relative low Fe^{2+} content, a Ca-rich type of diopside i.e. endiopside phase has been found. This period of quiescence is reflected by the pyroxene-knots composed of monoclinic pyroxenes mostly. After this second "stopover" the acidic pyroxene-andesite has solidified quickly in the area involved. This "frozen" state refering to a quick final cooling is reflected by the pigeonite [PANTÓ, G. 1964]. In the rocks of Hasdát-völgy showing marks of a thicker cover, even the alteration of the uralite can be observed. It transformed into chlorite, and the Ca-content released is fixed by small apatite needles in the centre of uralite and chlorite pseudomorphoses after pyroxenes.

In the foliated pyroxene-andesite characterized by more rapid ascension, the uralitization has not taken place. The only generation of the orthopyroxenes is the hypersthene of clino-character; and in presence of enough Fe^{2+} augite has formed, representing the monoclinic pyroxenes.

The pyroxene-andesites have involved inclusions consisting mainly quartz originating from the basement complex.

This fact accounts the more acidic character of the pyroxene-andesites attained likely in the crust. Originally, on the basis of their chemical composition the andesite could be pigeon-holed to the leucogabbroidic type of rocks defined by NIGGLI. Their more basic character is also corroborated by the presence of minerals such

hypersthene, bronzite, diopside and endiopside, though the latter three minerals could not have formed in the foliated pyroxene-andesite as a result of the more rapid ascension of the magma.

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SUBDIVISION OF THE UPPER PERMIAN SEQUENCE OF THE BÜKK MOUNTAINS IN NORTHERN HUNGARY

S. ANTAL

INTRODUCTION

Superficial occurrences of the marine Upper Permian in Hungary can be found only in the Bükk Mountains *(Fig. 1)*. Development and fossil content of them is stated by the fundamental publications of Z. SCHRÉTER and K. BALOGH. After these the sequence in question evolutes from its anhydrite- and gypsum-bearing, Gröden-type-footwall gradually and is overlayered conformably by light-coloured Lower Triassic limestones. The present preliminary report relaying on the basis of more detailed re-investigations enumerates the modifications of the former, hypothetically assumed stratigraphic column based principially on the distribution of the fossil assemblages.

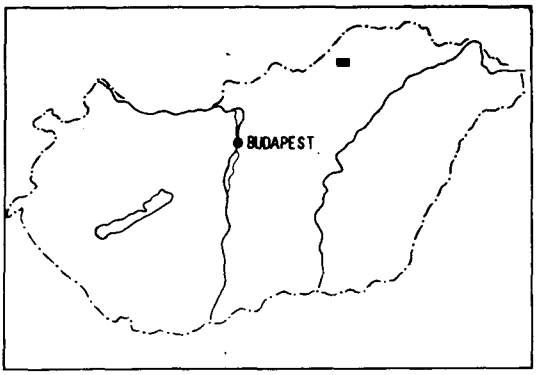

Fig. 1. Location of the superficial occurrences of the Upper Permian in Hungary.

METHODS

The undermentioned results are winned from the comparative research of the outcrops in the western proximity of the railway station Nagyvisnyó, and in the railway-cuts situated towards the ENE from here, further along the road of forestry on the eastern side of the Sebesvíz-valley (roughly 10 km distance off Nagyvisnyó towards the ESE). They are based on a bed-to-bed-sampling (on the average 1 sample/meter). Petrographic, paleontologic and tectonic observations on many other outrops aimed at the generalization of the results.

From the 91 samples collected between the foot and the hanging, a lot of surficial slides, thin sections, etched preparations, replicas, and calcite: dolomite determinations were carried out.

RESULTS

1. After summing up the data concerning the thickness of the different detail-profiles, the total thickness of the Upper Permian of the Bükk, estimated formerly to 200—250 m, must be modificated to 150 m. In spite of a little uncertainty caused by the covering with scree in some parts of the detail-profiles, this value may be raised with not more than 10—20 m.

2. In opposition to the former 6-member-subdivision of the sequence [BALOGH, K. 1964. p. 601], but observing its original delimitations towards the foot- and the hanging wall, respectively, the distinction of the following four, well characterized members is proposed:

Lower Trias

4. member:	Banded Limestone	10 m
3. member;	Dark limestones with intercalations of marl	55 m
2. member:	Dark limestones with *Waagenophyllum*	5—7 m
1. member:	Grey dolomites with intercalations of dark limestone	70 m

Beds of Gröden-type

The 1. and 4. member of this subdivision can be well correlated with the 1. and the 6. member of the former one, respectively. Considering the succession and the number of the intermediary members, however, the new subdivision differs considerably from the former one as follows:

a) Instead of two ones, only one horizon of *Waagenophyllum* could be established in the middle part of the sequence.

b) On the basis of the occurrence of *Waagenophyllum, Inozoa* (*Peronidella baloghi* FLÜGEL, H. W. 1973) and *Nautiloidea,* the formerly assumed high position of the beds of the railwaycut No. 5 rich in fossils (*Lyttonia, Tschernyschewia, clams, gastropods,* etc.) must have been ceased. Namely these beds have to be the equivalent of those of the "Mihalovits"-quarry. From that parallelization, however, a decrease of 50 m in the total thickness of the Upper Permian sequence results.

c) The dependence of the spreading of the calcareous *Algae (Gymnocodium, Mizzia, Permocalculus),* small foraminifers, brachiopods, clams and gastropods on the facies could be stated. These forms are namely to search only for restricted distances. Therefore they are inapplicable for an closer identification of the beds of different localities.

3. By studying the microfacies the following establishments could be verified:

a) the *1. member* consists of dolomicrite, dolosparite, bioclastite of wackestone-type, bioclastic micrite, sparry bioclastite and sparry mikbioclastite; all these build up altogether 13 bed groups, in the uppermost one with the first *Inozoans;* certain samples contain crystals of gypsum, too;

b) the *2. member* includes limestones bearing *Waagenophyllum, Inozoa* and in some places lenses of chert, too; usually, however, they are silicified only spottily, and consist of sparry, resp. coral-bearing bioclastite of packestone-type;

c) the *3. member* of variable composition build up of limestones and intercalated marls may be divided into 6 bedgroups consisting bioclastic micrite, micro-

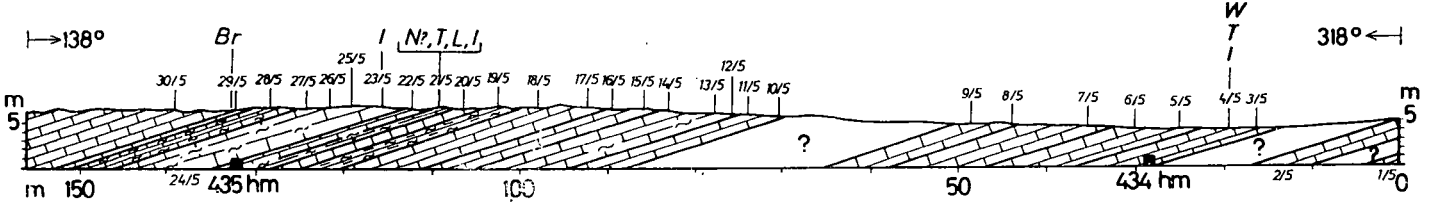

Fig. 2. Geologic section along the railway-cut No. 5 ENE of Nagyvisnyó. — Legends at Fig. 3.

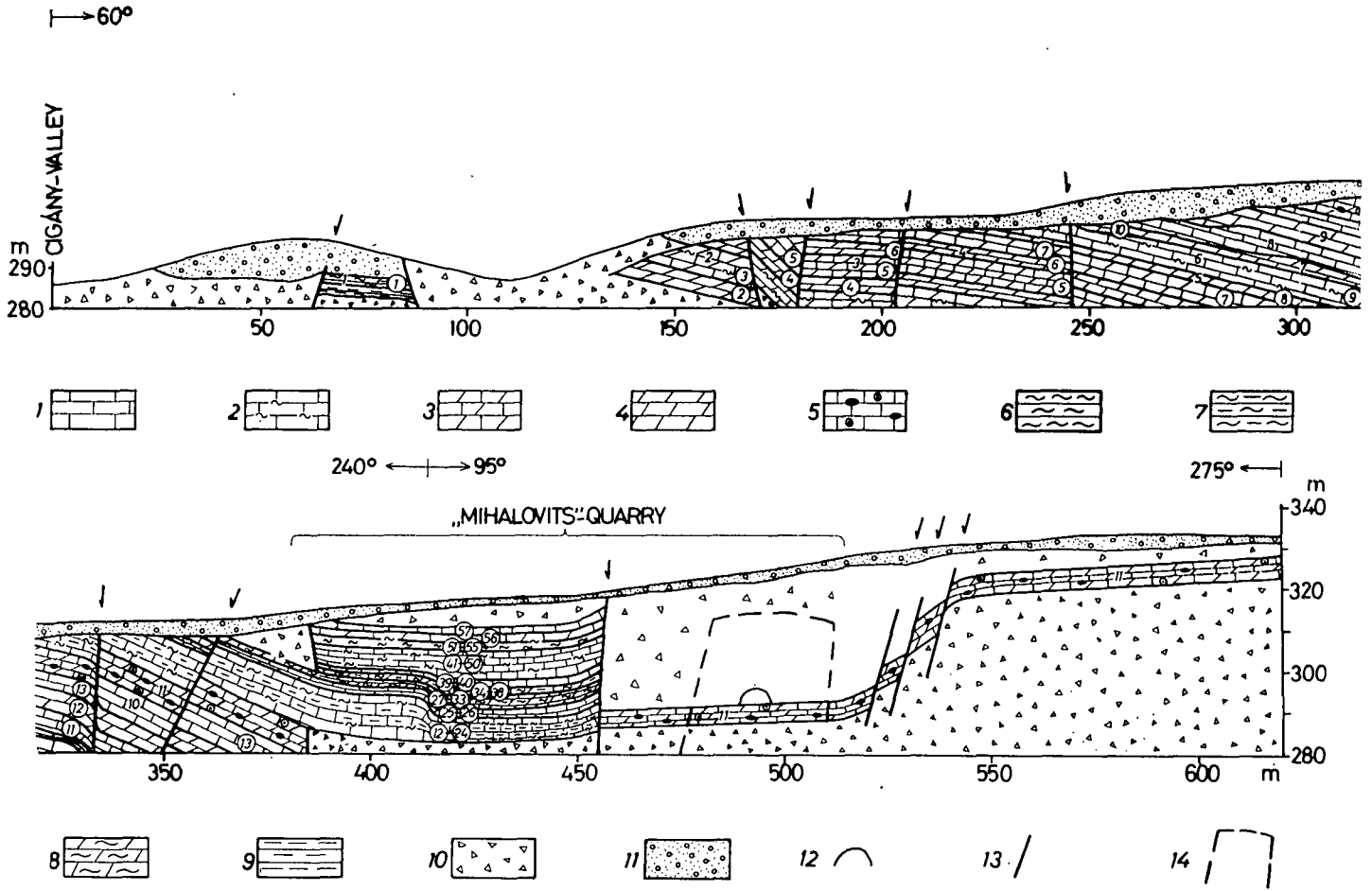

Fig. 3. Geologic section between the Cigány-valley and the railway station Nagyvisnyó. *1.* Limestone. *2.* Limestone interbedded by calcareous marl. *3.* Dolomitic limestone. *4.* Dolomite. *5.* Limestone with *Waagenophyllum* and lenses of chert. *6.* Dolomitic calcareous marl. *7.* Clayey mar. *8.* Dolomitic marl. *9.* Shale. *10.* Scree. *11.* Miocene sandstone and conglomerate. *12.* One-time depot of explosive. *13.* Fault. *14.* Smaller quarry. *I:* Inozoans. *L:* Lyttonia. *T:* Trilobite. *W:* Waagenophyllum. *N:* Nautiloids. *Br:* Brachiopods. *hm:* Railway-point. *?:* Covered part of the sectionl. *Numbers in circle:* Serial numbers of the bed groups. *Simple numbers:* Places of sampling.

sparry micrite, bioclastic sparite, micritic bioclastite, micritic pelletite, sparry biomicrite, sparry mikbioclastite, calcareous marl, dolomite-bearing and dolomitized calcareous marl, dolomitized and dolomite-bearing marl, further clayey marl;

d) the *4. member* build up of banded limestones consists of micrite with microsparry lamelles and contains sometimes dolosparry ooids, too;

e) the Upper Permian of the Bükk originated in <40 m depth in a less ventillated part of the sublitoral region;

f) the agitation of water became more vivacious only during the building-up of the banded, poor-in-fossil, but oöide-bearing limestones of the uppermost part of the sequence in question; the latters continue without break in the more lighter limestones of the Lower Triassic consisting of similarly laminated micritic oosparite, resp. oöide-bearing sparite. The boundary between the Upper Permian and Lower Triassic may be drawn only by the help of the disappearence both of the calcareous algae, crinoid fragments, and the dark colours, because the first beds of the Lower Triassic transgression are entirely free from fossils.

5. Up to the present day the Upper Permian of the Bükk furnished only rare and specifically undeterminable rests from the group of the *Fusulinids* (*Staffella* sp., *Reichelina* sp., *Codonofusiella* sp.).

The succession of the macrofossils collected from bedrock:

Railway-cut No. 5 (Fig. 2):

2. member (in the vicinity of the hectometer No. 434): *Inozoa, Waagenophyllum* sp., *Pseudophillipsia hungarica* SCHRÉTER.

3. member, Lyttonia-bed (at the hectometer No. 435): *Peronidella baloghi* FLÜGEL, H. W., *Lyttonia nobilis* (WAAGEN), *Pseudophillipsia hungarica* SCHRÉTER, *Pseudorthoceras cyclophorum* (WAAGEN) (?).

3. member, cca. 5 m above the *Lyttonia*-bed: a rich association of brachiopods with *Tschernyschewia* [V. BALOGH, K. 1964. pp. 596—597; SCHRÉTER, Z. 1963].

"Mihalovits"-quarry (Fig. 3):

1. member, 13. bed group, 10. sample: *Inozoa.*

2. member, 11. sample: *Waagenophyllum (Waagenophyllum) kueichowense* HUANG (or *W. (W.) huangi* Douglas).

3. member, 17—19. sample: *Pseudorthoceras cyclophorum* (WAAGEN).

Eastwards from the Sebesvíz-valley, along the lower road of forestry (Fig. 4):

2. member: Waagenophyllum kueichowense Huang (or. *W. (W.) huangi* Douglas).

3. member (cca 42 m distance from the former one, in a place plotted in the profile on basis of the *Inozoa*-bearing scree): *Inozoa.*

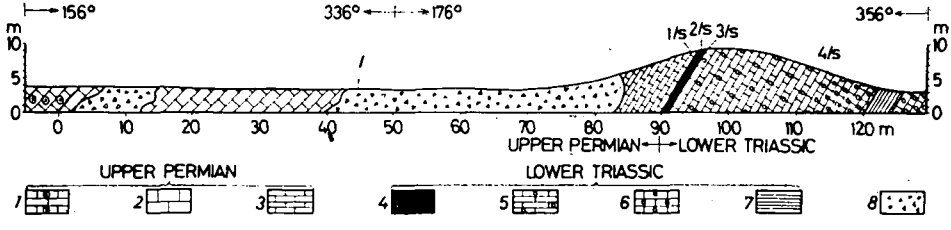

Fig. 4. Geological section along the lower road of forestry in the Sebesvíz-valley.
1. Limestone with *Waagenophyllum. 2.* Limestone. *3.* Banded limestone. *4.* Shaly marl. *5.* Limestone containing a few oöides. *6.* Oöidic limestone. *7.* Laminated limestone and shale. *8.* Scree. *1/S, 2/S:* Places of sampling.

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ON THE OCCURRENCE OF PRIMARY DOLOMITES IN QATRANI FORMATION (OLIGOCENE) IN FAYOUM PROVINCE, WESTERN DESERT, EGYPT

A. M. ABDEL REHIM and M. R. ABDEL-KIREEM

ABSTRACT

This work represents a study of petrographic properties, differential thermal analysis and *x*-ray diffraction study of carbonate rocks of the Qatrani formation of Oligocene age in Fayoum Province, Egypt. These carbonate rocks can be grouped into three major textural and compositional types. Microcrystalline dolostones or dolomicrite, gypsiferous dolomicrite and dolomitic sandstones.

INTRODUCTION

Thin dolostones and dolomitic rocks are interbedded with shales, sandstones and gypsum in the Qatrani Formation, 618 feet in thick (Oligocene), in Fayoum Province, Egypt. The thickness of these bands ranges from one foot to 8 feet; that of the interbedded terrigenous sediments from one foot to 48 feet.

In addition, quartz grains are disseminated throughout many of the dolostones, all variations are present from nearly pure dolostones with a few scattered quartz grains to dolomitic sandstone.

The present paper describes the petrographic properties of the carbonate rocks from the Qatrani Formation of Oligocene age in Fayoum Province, in addition to differential thermal analysis, x-ray diffraction and chemical analysis. The purpose of this work to show that the dolostones are of primary or secondary in origin. It is hoped that this study will shed more light on the nature of this carbonate rocks. *Fig. 1* shows the location of Gebel Qatrani.

STRATIGRAPHY AND GENERAL LITHOLOGY

The Quatrani Formation was established by BEADNELL [1905] to represent the fluviomarine sediments below the basalt and above the Kasr El Sagha Formation (Upper Eocene) exposed at the Gebel Qatrani, Fayoum Province, Egypt. The formation is predominantly a terrigenous unit with eight dolomite bands. The detailed stratigraphy and lithology of the formation has been discussed by BEADNELL [1905], BLANCKENHORN [1921], CUVILLIER [1926] and recently by ISMAIL and ABDEL-KIREEM [1971*a* &*b*].

The Qatrani Formation (Oligocene) is represented by a section 618 feet thick, exposed at Gebel Qatrani, composed of 40.05% sandy shales, 18.4% sandstones, 15.0% shales, 7.36% calcareous sandstones, 2.95% gypsiferous shales, 3.7% dolostones, 1.29% dolomitic sandstones, 0.27% sandy marls, 0.2% gypsum, and 10.7 % basal as a sheet capping the whole formation [ISMAIL and ABDEL KIREEM 1971*a*]. The succession is only fossiliferous with a rich vertebrate fauna, in addition to silicified wood fragments.

METHODS OF STUDY

Eighty five samples from the Qatrani Formation were collected, unfortunatly only eight samples are of dolomites. These dolostones and dolomitic rock samples were thin sectioned, about 40 thin section were prepared for a detailed petrographic analysis. The rock samples were chemically analysed for the determination of insoluble residue, R_2O_3 ($=Fe_2O_3+Al_2O_3$), CaO, MgO, slouble Cl^-, in addition to the Ca/Mg ratios. Minerals of sediments of Qatrani Formation were studied by differential thermal analysis and x-ray diffraction.

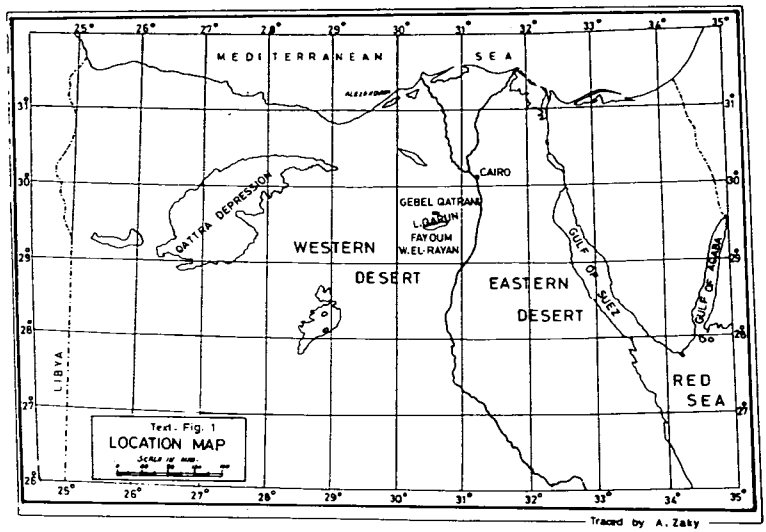


Fig. 1.

PETROGRAPHY AND CARBONATE NOMENCLATURES

The carbonate rocks at Qatrani Formation can be grouped for descriptive purposes to three major textural and compositional types which are:

1) Microcrystalline dolostone or dolomicrite.
2) Gypsiferous dolostone (dolomicrite).
3) Dolomitic sandstone.

It is emphasized that these classes are rather arbitrary and set up for convenience: all transitions between first and third classes are present.

Type 1: Microcrystalline dolostone or dolomicrite (Plate I—II, 1—5): In this category are those dolostone rocks containing not less than 16.7% MgO, comprising samples No. 3Q, 46Q, 61Q, 72Q and 76Q.

These microcrystalline dolostones alternates with zones of red shales, sandstones and gypsum. Hematitic material is in almost all rocks of this class and mostly in amounts about 7% except for the first dolostone band 3Q. They all show nearly similar petrographic characters, generally with much coarse grained quartz. The quartz grains are angular to subrounded and are embedded in a microcrystalline dolomitic matrix of uniform textures. Abundant oval to rounded cavities filled with dolomites are present in some thin sections represented by samples 46Q, 61Q and 72Q. Clay exists in some beds but mostly in minor amounts.

Type 2: Gypsiferous calcitic magnesit (Plate II, 6—7): In this class are rocks containing "layered" and void filling gypsum which is intimately associated with the

fine grained magnesite. This calcitic magnesite alternate with zones of brown to red shales, yellow to red sandstone and gypsiferous shales. This type is represented by samples No. 38Q and 63Q. Hematitic materials are generally present, the thin sections are deeply stained by this hematitic materials. Abundant fine to coarse quartz grains scattered throughout the matrix.

This microcrystalline calcitic magnesite rock is interlaminated and intermixed irregularly with the gypsum.

On the origin of "layered" gypsum, MURRAY [1954] suggested that it may be due to precipitation and sedimentation in a standing body of water subjected to continuous evaporation.

Type 3: Dolomitic sandstone (Plate II, 8): Dolomitic sandstone constitutes a relatively thick bed (8 feet thick) of the Qatrani Formation relative to the other dolomitic beds. This type is represented by sample No. 73Q. The quartz sand which constitute about 51% are angular to subrounded, ill-sorted and size range from 0.02 mm to 20.0 mm. This detrital material was derived from an older sediment, most probably the Upper Eocene Kasr El Sagha Formation.

The ferric oxide mineral hematite and the ferric hydroxide mineral (?) limonite are respectively responsible for the red and brown colors of the Qatrani Formation considered in this study. Although hematite is the dominant ferric mineral, considerable limonite is also present and the coexistence of the two minerals, often found together within single zones in dolomite rhombohedra suggests that much of the hematite may have resulted from the partial dehydration of original limonitic zones. Most of the limonite and hematite occurs either finely dispersed through dolomite (*Plate I—II, 2, 6 & 7;* samples 46Q, 38Q and 63Q respectively) or as concentrated zones in dolomite rhombohedra (*Plate II, 5,* sample 76Q).

EXPERIMENTAL WORK

Some of sediments, mainly carbonates of the Qatrani Formation were subjected to differential thermal analysis and *x*-ray diffraction.

Techniques of work:

Differential thermal analysis procedure: Differential thermal analysis were carried out for the 8 carbonate samples from Qatrani Formation. These samples were chosen to reflect the different types of carbonate in the whole formation. The samples were ground to -200 mesh.

Differential thermal analysis technique: Differential thermal analysis experiments were carried out by using F. PAULIK, J. PAULIK and L. ERDEY derivatograph. This apparatus records simultaneously four thermal curves: (T) the change of temperature of the sample, (DTA) differential thermal analysis, (TG) thermogravimetric, (quantitatively in mg) and (DTG) derivative thermogravimetric, on a single sample under controlled conditions. DTA and temperature measuring thermocouples are Pt/Pt-Rh wires. Ceramic crucible and a ceramic sample holder were used. Alumina, calcinated at 1000 °C was used as a reference material. The parameters during tests were as follows: weight of sample 1 g, T-1200 °C, DTA-1/10, 1/20, DTG-1/10, TG-500 mg and heating rate of 10 °C per minute. All determinations were carried out in air atmosphere.

X-ray diffraction analysis procedure: A Siemens Crystalloflex diffractometer was used with nickel filtered copper radiation. Exposure was one hour and scanning speed was $1°\ 2\Theta$ per minute, at 1 cm per minute chart speed. Intensities were collected to maximum $2\Theta = 65°$. The sensitivity of the experiment was 1×10 impl./min., and the statistical error was 1.5%.

RESULTS AND DISCUSSIONS

The results obtained for DTA of carbonate sediments of Qatrani Formation (Oligocene), Fayoum Province are given in Table 1 and graphically shown in *Fig. 2.*

On the basis of DTA results the carbonate minerals of Qatrani Formation could be grouped into:

1) Dolomite—Calcite—Magnesite associations represented by samples 3Q, 46Q, 61Q, and 76Q.
2) Magnesite—Calcite—Dolomite associations represented by sample 72Q.
3) Gypsum—Magnesite—Calcite associations represented by samples 38Q and 63Q.

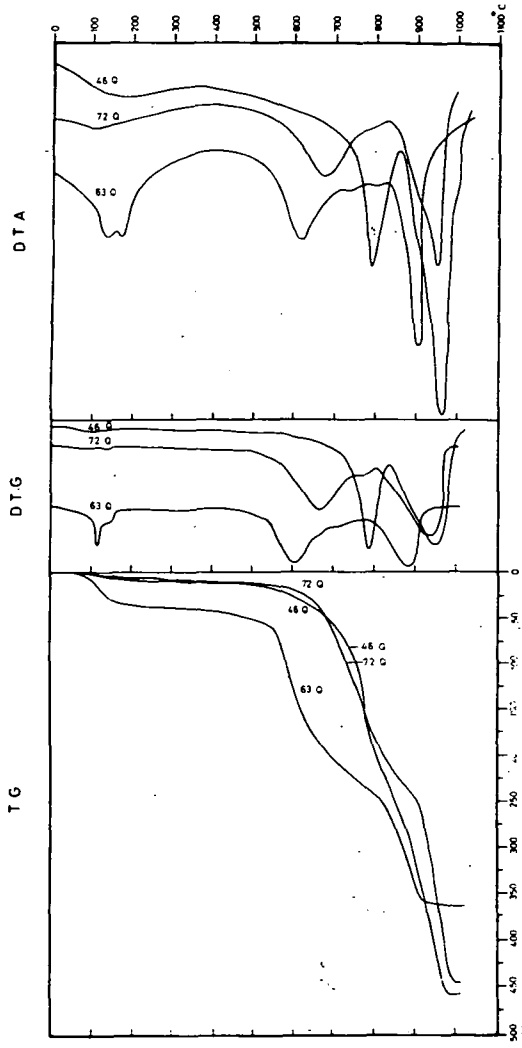


Fig. 2. DTA, DTG and TG curves for three representative carbonate samples from Qatrani Formation, Fayoum

TABLE 1

Chemical Composition of Carbonate Sediments of Qatrani Formation.
(Data obtained from DTA and Chemical Analyses are tabulated.)

Sample No.	Analysis	CaO in Calcite	CaO in Dolomite	Total CaO %	MgO in Magnesite	MgO in Dolomite	Total MgO %	Calcite %	Magnesite %	Dolomite %	R_2O_3 %	Insoluble Residue %	H_2O %	Total %	Gypsum %	Ca/Mg ratio	Cl^- ppm
76Q	DTA	4.98	13.50	18.48	12.48	9.84	22.32	8.87	26.22	44.41	7.28	12.19	1.10	100.07	—	0.98	
	Chemical			18.30			22.41				7.13	12.29	1.10				1355
73Q	DTA	0.33	13.29	13.62	1.92	9.6	11.52	0.58	3.80	43.66	2.04	50.04	0.50	100.62	—	1.40	
	Chemical			14.02			11.11				2.00	49.35	0.50				250
72Q	DTA	20.62	4.52	25.14	18.7	3.19	21.89	36.70	38.95	14.67	7.06	2.28	0.50	100.16	—	1.36	
	Chemical			24.63			21.97				7.11	2.25	0.50				220
63Q	DTA	14.56	3.47	18.3	14.16	2.54	16.70	25.91	29.45	11.55	11.34	18.24	3.5	99.99	17.2	1.28	
	Chemical			17.81			16.81				11.31	18.32	3.5				1904
61Q	DTA	8.22	22.07	30.29	2.83	15.88	19.05	13.68	6.08	72.59	6.54	1.04	0.8	100.73	—	1.88	
	Chemical			30.01			20.01				6.11	1.00	0.8				308
46Q	DTA	5.29	24.70	29.99	1.1	17.76	18.86	9.42	2.28	81.21	5.5	1.16	0.5	100.07	—	1.88	
	Chemical			30.03			18.51				5.1	1.07	0.5				332
38Q	DTA	24.14	—	24.14	9.93	—	9.93	42.96	18.60	—	10.36	24.04	4.0	99.96	11.4	2.88	
	Chemical			24.00			10.03				9.76	23.81	4.0				5992
3Q	DTA	3.79	26.00	29.79	2.28	18.72	21.00	6.74	4.75	85.55	0.65	3.08	0.7	101.47	—	1.68	
	Chemical			29.73			21.00				0.65	3.00	0.7				325

Dolomite—Calcite—Magnesite association

This association is represented by sample No. 46Q, *Fig. 2* .The dolomite forms the major mineral constituent (44.1% up to 84.15%) with considerable amounts of calcite (6.77%—13.68%) and magnesite (2.28%—26.22%).

The T curve is generally smooth and has a gentle slope with slight concavities at 800 °C and 950 °C reflecting the dissociation of dolomite and $CaCO_3$ respectively. The DTA curve shows two sharp endothermic peaks. The first at 800 °C corresponding to the decomposition of dolomite into MgO and $CaCO_3$. The second peak at 950 °C is large and sharp representing the decomposition of $CaCO_3$. The DTG curve shows similar peaks as DTA curve but at lower temperature than DTA peaks (790 and 940 °C respectively). The TG curve is generally smooth with gentle slope downward up to temperature 580 °C, then drop suddenly showing loss of CO_2 in two stages. The first stage represents loss of CO_2 due to decomposition of dolomite, the second stage represents loss of CO_2 due to the dissociation of $CaCO_3$.

TABLE 2

Differential thermal analyses of carbonate samples of Qatrani Formation
(Weight of sample 1000 mg, Heating rate 10 °C/min.)

Sample No.	DTA curve		DTG Curve		Loss mg.
3Q	Slight end peak at	100 °C			
	Sharp & large end peak	810 °C	Sharp & large end peak	780 °C	230
	Sharp & large end peak	950 °C	Wide & large end peak	930 °C	227
38Q	Wide end peak at	140 °C	Small end peak at	120 °C	25
	Wide & large end peak	630 °C	Wide & large end peak	625 °C	98
	Sharp & large end peak	920 °C	Wide & large end peak	910 °C	191
46Q	Sharp & large end peak	795 °C	Sharp & large end peak	785 °C	210
	Sharp & large end peak	950 °C	Wide & large end peak	938 °C	233
61Q	Slight wide end peak	120 °C			
	Sharp & large end peak	780 °C	Sharp & large end peak	770 °C	210
	Sharp & very large end peak	940 °C	Wide & large end peak	920 °C	235
63Q	Double end peak	140 °C	Small end peak	120 °C	35
	Wide & large end peak	610 °C	Wide & large end peak	600 °C	155
	Slight end peak at 730—	800 °C	Slight end peak	720 °C	28
	Large & sharp end peak	900 °C	Wide & large end peak	890 °C	140
72Q	Slight end peak	110 °C			
	Wide & large end peak	670 °C	Wide & large end peak	660 °C	205
	Slight end peak	780 °C	Slight end peak	778 °C	35
	Sharp & large end peak	935 °C	Wide & large end peak	922 °C	195
73Q	Sharp & large end peak	790 °C	Sharp & large end peak	787 °C	100
	Sharp & large end peak	940 °C	Wide & sharp end peak	910 °C	79
76Q	Wide end peak	630 °C	Wide end peak	620 °C	138
	Sharp & large end peak	820 °C	Sharp & large end peak	815 °C	108
	Sharp & large end peak	940 °C	Wide & large end peak	910 °C	142

Magnesite—Calcite—Dolomite association

Represented by *Fig. 2* for sample No. 72Q. This association shows large amounts of magnesite (38.95%) and calcite (37.07%) and small amount of dolomite (14.36%).

The T curve is generally smooth with gentle slope with slight concavity at 650 °C reflecting the dissociation of magnesite and large concavity at 940 °C indicating the decomposition of $CaCO_3$. The DTA curve shows three endothermic peaks. The first is large at 670 °C for the decomposition of free magnesite. The second peak is small at 780 °C corresponding to the dissociation of dolomite. The third is large and sharp at 940 °C corresponding to the dissociation of $CaCO_3$ as free calcite and that resulting from the decomposition of dolomite. The DTG curve shows similar peaks as DTA curve but at lower temperature (660°, 775°, 925°C respectively).

The TG curve is generally smooth with gentle slope downwards up to 460 °C and shows loss of CO_2 in three stages. The first stage indicates loss of CO_2 due to decomposition of magnesite, the second stage due to dissociation of dolomite and the third stage due to the decomposition of $CaCO_3$.

Gypsum—Magnesite—Calcite association

This association represented by sample No. 63Q in *Fig. 2*. The calcite and magnesite forms the major constituent of this association. Also, it is distinguished by the presence of gypsum in considerable amounts (11.47%—17.21%).

The T curve is smooth with gentle slope except for slight concavities at 620 °C and 920 °C due to the decomposition of magnesite and $CaCO_3$ respectively.

The DTA curve shows four endothermic peaks. The first is double peak at 140 °C characteristic for gypsum. The second is large at 610 °C due to decomposition of magnesite. The third is smooth and at 750 °C representing dissociation of dolomite. The fourth is sharp and large at 940 °C representing the dissociation of $CaCO_3$.

The DTG curve shows similar peaks as DTA curve but at lower temperature.

TABLE 3

X-ray powder diffraction data of sandstone α-quartz
(Sample: 50 Q)

d (Å) ASTM	*d*(Å) Observed	I ASTM	I Observed	*hkl*
4.260	4.277	35	35	100
3.343	4.344	100	100	101
2.458	2.460	12	14	110
2.282	2.284	12	11	102
2.237	2.242	6	6	111
2.128	2.133	9	10	200
1.980	1.985	6	7	201
1.817	1.821	17	15	112
1.801	1.812	<1	<1	003
1.672	1.678	7	7	202
1.659	1.661	3	3	103
1.608	1.609	<1	1	210
1.540	1.545	15	15	211
1.453	1.451	3	3	113

TABLE 4

X-ray powder diffraction data of dolomite
(Sample: 46 Q)

d(Å) ASTM	*d*(Å) Observed	I ASTM	I Observed	*hkl*
4.030	4.052	3	3	101
3.690	3.713	5	8	012
2.896	2.903	100	100	104
2.670	2.680	10	9	006
2.540	2.542	8	7	015
2.405	2.413	10	13	110
2.192	2.195	30	43	113
2.066	2.072	5	5	021
2.015	2.022	15	22	202
1.848	1.852	5	12	024
1.804	1.809	20	26	018
1.780	1.790	30	31	116
1.567	1.570	8	5	211
1.545	1.547	10	8	122
1.490	1.497	1	1	1010
1.465	1.467	5	7	214
1.445	1.446	4	5	028

TABLE 5

X-ray powder diffraction data of calcite
(Sample: 46 Q)

d(Å) ASTM	*d*(Å) Observed	I ASTM	I Observed	*hkl*
3.860	3.863	12	8	102
3.035	3.038	100	100	104
2.845	2.847	3	3	006
2.495	2.494	14	12	110
2.285	2.285	18	18	113
2.095	2.095	18	16	202
1.927	1.927	5	6	204
1.913	1.913	17	18	108
1.875	1.875	17	18	116
1.626	1.627	4	3	211
1.604	1.605	8	7	212
1.587	1.588	2	2	1010
1.525	1.527	5	4	214
1.518	1.519	4	3	208
1.510	1.509	3	2	119
1.473	1.473	2	2	215
1.440	1.441	5	5	300

TG curve shows losses in four stages. The first is that a loss of held water in gypsum. The second stage represents loss of CO_2 due to dissociation of magnesite. The third stage shows loss of CO_2 due to decomposition of dolomite. The fourth stage indicates loss of CO_2 due to dissociation of $CaCO_3$.

The *x*-ray study of representative samples of sediments of Qatrani Formation shows that the sandstone consists mainly of quartz with some kaolinite. All carbonate

TABLE 6

X-ray powder diffraction data of kaolinite
(Sample: 70 Q)

d(Å) ASTM	*d*(Å) Observed	I ASTM	I Observed	*hkl*
7.170	7.178	100	100	001
4.478	4.473	35	80	020
4.366	4.368	60	70	$1\bar{1}0$
4.186	4.180	45	60	$11\bar{1}$
4.139	4.140	35	34	$1\bar{1}\bar{1}$
3.847	3.848	40	40	$02\bar{1}$
3.745	3.747	25	25	021
3.579	3.588	80	70	002
3.376	3.384	35	34	111
3.155	3.165	20	20	$11\bar{2}$
3.107	3.116	20	20	$1\bar{1}2$
2.754	2.774	20	20	022
2.566	2.564	35	50	$1\bar{3}0,20\bar{1}$
2.553	2.553	25	40	130
2.535	2.538	35	36	$13\bar{1}$
2.495	2.500	45	45	$1\bar{3}1,200$
2.385	2.392	25	22	003
2.347	2.355	40	40	$20\bar{2}$
2.338	2.337	40	42	$1\bar{3}1,11\bar{3}$
2.293	2.273	35	30	131
2.253	2.256	20	22	$13\bar{2}$
2.197	2.198	20	14	$1\bar{3}\bar{2}$
2.186	2.187	20	14	$201,2\bar{2}0$
2.133	2.129	20	16	$02\bar{3}$
2.064	2.036	20	10	$2\bar{2}\bar{2}$
1.997	1.994	35	34	$20\bar{3}$
1.987	1.982	35	32	$1\bar{3}2$
1.974	1.976	20	14	$2\bar{2}1$
1.952	1.954	20	16	221
1.939	1.946	35	20	132
1.921	1.927	20	14	$1\bar{1}3,04\bar{2}$
1.897	1.899	25	20	$13\bar{3}$
1.870	1.868	20	16	042
1.845	1.857	25	20	$1\bar{3}3$
1.838	1.841	35	30	$202,22\bar{3}$
1.810	1.808	20	14	$11\bar{4},22\bar{3}$
1.789	1.794	25	20	004
1.710	1.731	25	22	$2\bar{2}2$
1.689	1.697	25	22	$24\bar{1}$
1.681	1.685	25	22	$150,15\bar{1}$
1.669	1.672	40	40	$2\bar{4}0,20\bar{4}$
1.660	1.661	40	30	$1\bar{3}3,240$
1.649	1.653	40	30	$3\bar{1}2$
1.633	1.628	30	24	$3\bar{1}0,24\bar{2}$
1.620	1.621	70	60	$1\bar{5}1,133$
1.607	1.614	30	24	$2\bar{4}2,043$
1.586	1.592	60	30	$13\bar{4}$
1.553	1.556	30	24	$2\bar{2}4,\ 241$
1.545	1.542	40	36	$1\bar{3}4,3\bar{1}3$
1.537	1.538	40	36	203
1.489	1.489	90	40	$33\bar{1},33\bar{1}$

sediments contain dolomite. The *x*-ray peaks of calcite and dolomite minerals, constituting the main composition of carbonate sediments and quartz of sandstone are narrow and sharp, suggesting good crystallinity. The *x*-ray data of mineral constituents of Qatrani Formation are given in Tables 3, 4, 5 and 6 and they are consistent with literature data.

The microscopic study of mineral constituents of sediments of Qatrani Formation is in a good agreement with *x*-ray powder diffraction study and differential thermal analysis.

CONCLUDING REMARKS

From the above study of the dolomite samples from the Qatrani Formation, the following evidences and observations can be seen:

1) The dolomites are generally finely micrograined, micrite (*Plate I—II, 1, 3* and *5*).
2) Commonly aphanitic to finely crystalline, with uniform texture (*Plate I—II, 2, 4* and *8*).
3) Most of them are brecciated (*Plate I—II, 3—5* and *8*).
4) Most of them have admixed clay and fine silt.
5) Associated with anhydrite and gypsum bands.
6) Some of the carbonates are interfingered with gypsum, sample 38Q, 63Q *(Plate II, 6—7)*.
7) Contain no relic limestone textures.
8) All the formation are red shales, sandstones, and siltstones with the dolomite interbedded bands.

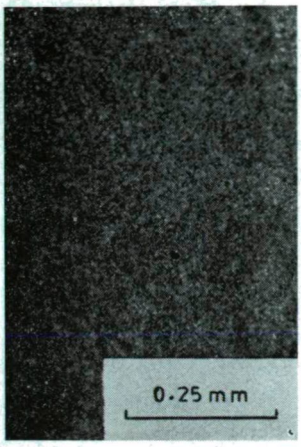
LEIGHTON and PENDEXTER [1962], BISSEL and CHILINGER [in CHILINGER *et al.* editors, 1967] considered a genetic origin for the dolomite for the above evidences.

Most of the Qatrani dolomites are associated and interbedded with evaporite sediments, typically of very fine-grained show uniform texture, lack obvious textural features that indicate origin by replacement of $CaCO_3$ sediments. Such dolostones indicates a primary origin by many authors [TARR, 1919; CLOUD and BARNES, 1948; COOPER, 1956; DUNBAR and RODGERS, 1957; KRYNINE, 1957; ILLING, 1959; HAM, 1966, and others].

COOPER [1956] considered the Knox dolostones of the Cambro-Ordovician rocks in the central Appalachian of Virginia, U.S.A., as primary in origin. Because the formation lacks limestones and includes beds of chert and numerous interbeds of quartz sandstones, a similar condition that were observed in the Qatrani Formation.

BISQUE and LEMISH [1959], recorded direct correlation of higher proportion of dolomite with greater insoluble contents in the Cedar Valley Formation (Devonian) of Iowa. A similar characteristics are postulated from the present study. The same relationship between dolomite and insoluble content was found by CHILINGER [1956], MURRAY [1960] and SCHMIDT [1964].

WEBER [1964], discussed the relationship between the water soluble chloride and the environmental conditions, he concluded that rocks deposited under marine condition must contain more than 35 ppm chloride ion. The Qatrani dolomites contain high amount of soluble chloride ions ranging from 308—6000 ppm (see Table 1), which indicates a higher water salinity of probably lagoonal conditions and the occurrence of evaporites.



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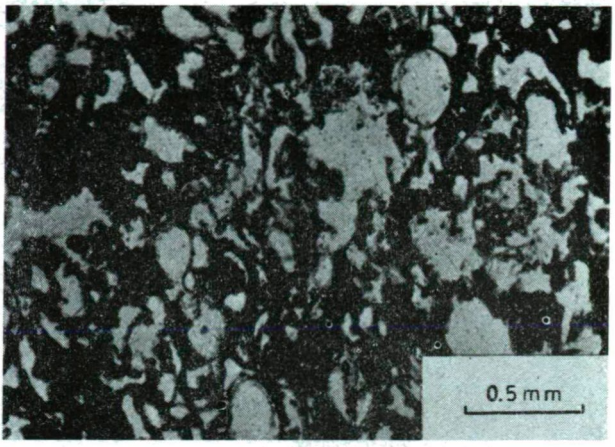

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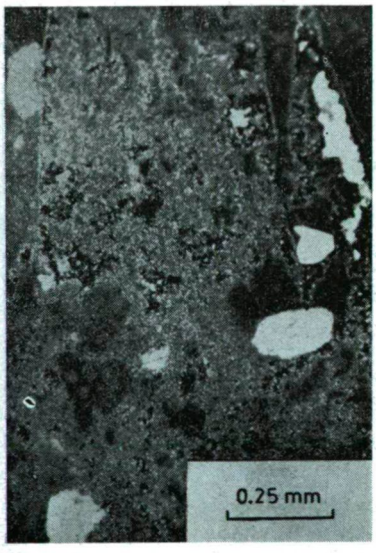

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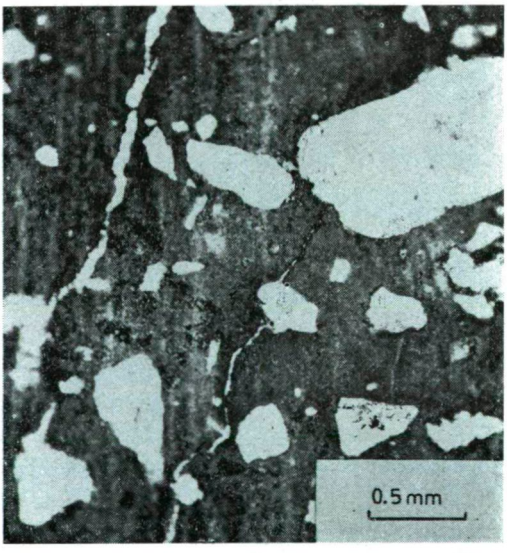
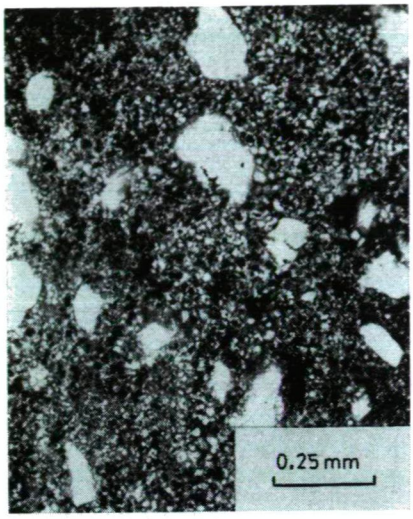


4

EXPLANATION OF PLATES

PLATE I

1. Microcrystalline dolostone (dolomicrite), consisting of microcrystalline dolomites of uniform texture. Sample 3Q, Qatrani formation, Oligocene.
2. Microcrystalline dolostone (ostracodes dolomicrite), consisting of microcrystalline dolomites, deeply iron-stained originally; with abundant ostracodes tests, filled with dolomicrites secondary after micrite.The unstained ostracode tests are clearly deposited after the formation of the original rock-mother the dolomites.Sample 46Q, Qatrani formation, Oligocene.
3. Microcrystalline dolostone (sandy dolomicrite), consisting of microcrystalline primary dolomites. Fine-grained dolomites is a diagenetic after the primary dolomicrite. Sample 61Q, Qatrani formation, Oligocene.
4. The same. Rock shows considerable porosity, sample 72Q, Qatrani formation, Oligocene.



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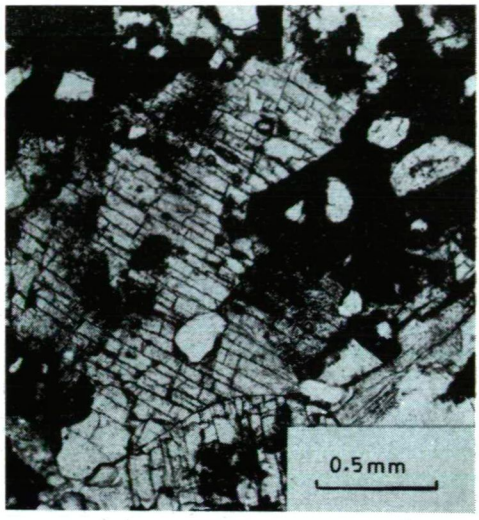

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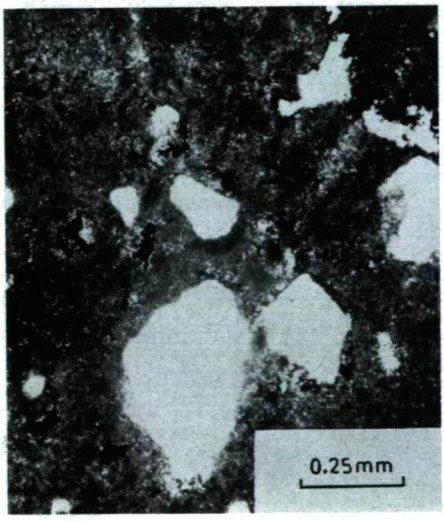

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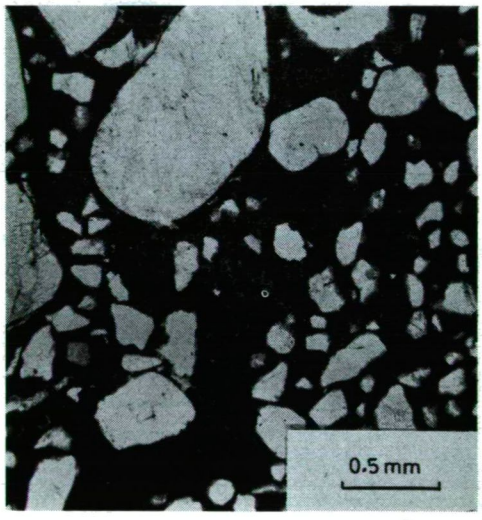

8

PLATE II

5. Crystalline dolostone (sandy dolosparite), consisting of very fine crystalline dolomite rhombs (idiotopic dolomite), deeply iron-stained, with abundant angular to subangular, coarse-grained quartz, sample 76Q, Qatrani formation, Oligocene.
6. Gypsiferous calcitic magnesite, consisting of microcrystalline, undifferentiated calcitic magnesite interlaminated and intermixed irregularly with gypsum. Hematitic materials are abundant. Sample 38Q, Qatrani formation, Oligocene.
7. The same, with abundant, coarse angular quartz grains. Sample 63Q, Qatrani formation, Oligocene.
8. Dolomitic sandstone, consisting of abundant, angular to subrounded, ill-sorted (size ranging from 0.02 mm. to 20 mm.) quartz detrital grains in a microcrystalline dolomites, partly iron-stained. Sample 73Q, Qatrani formation, Oligocene.

This conditions are more favorable for the formation of syngenetic dolomites.

From the above discussions, it can be concluded that the dolomites of Qatrani Formation may be probably of primary origin. The observed characteristics of Qatrani dolomites are consistent with the literature evidences of those of primary origin.

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SOME PROBLEMS ON THE MANGANESE ORES OF ANDHRA PRADESH

J. S. R. KRISHNA RAO

INTRODUCTION

The author summarizes his experiences with manganese ores of Andhra Pradesh, over 25 years. Manganese ore of the former Vishakhapatnam district was reported in 1858 during the laying of the railway track by Britishers. Subsequently FERMOR [1909], a Geological Survey of India official described the deposits in his manganese memoir. The Visakhapatnam deposits were of academic interest also, because, FERMOR classified them as secondary, formed from magmatic manganese rich rocks named by him as '*kodurite*' which according to him occurs typically at Koduru, intrusive into the khondalite series. Fermor suggested kodurite as a suit of rocks rich in manganese content showing differentiation crystallization trends, characteristic of magmatic products. But when he classified them according to C. I. P. W., he had to provide new minerals like tephrite in the C. I. P. W. Norm. CROSS and latter FERMOR [1915] suggested that the manganese deposits of Visakhapatnam district were formed by alteration of hybrid rocks which are formed when granites intruded into the manganese bearing sediments in the area.

Since, the Geology Department of Andhra University took interest in the above mentioned problem and worked on manganese ores of Koduru and adjoining areas where similar features were shown by manganese ores. RAO [1948] worked and stated that the parentage of manganese ores is a hybrid rock rich in manganese. The field observations by various people not only at Koduru and Garbham but also in other places like Chipurupalle, Gotivada, Kottakarra, Ramabadhrapuram, Rayagada, Andra brought out conclusions that the association of the khondalite and manganese is a fact and that the manganese ores generally follow the trends of the khondalites. Manganese ores or manganese bearing rocks do not show any intrusive nature or contacts with khondalites in the area. They sometimes show lenticular bands pinching off along strike, and are folded and faulted similar to the khondalite series and hence be considered as syngenetic and syntectonic with the khondalite series. More and more observations have been made as mining expanded, and it is observed that the manganese ores occur as beds and follow a NE—SW trend (general strike direction of the khondalites), generally show folding symmetric/asymmetric, plunging folds etc. Further, the manganese bearing area being vast and stratigraphically being the oldest much confusion is introduced due to latter metamorphism and metasomatism, with the result, a continuous tracing of the manganese bands is hampered. The khondalite series of rocks and manganese ores which are closely and intimately associated show cross folding and at many places are traversed by pegmatitic veins, quartz lenses, secondary ore veins, thus complicating the structural features.

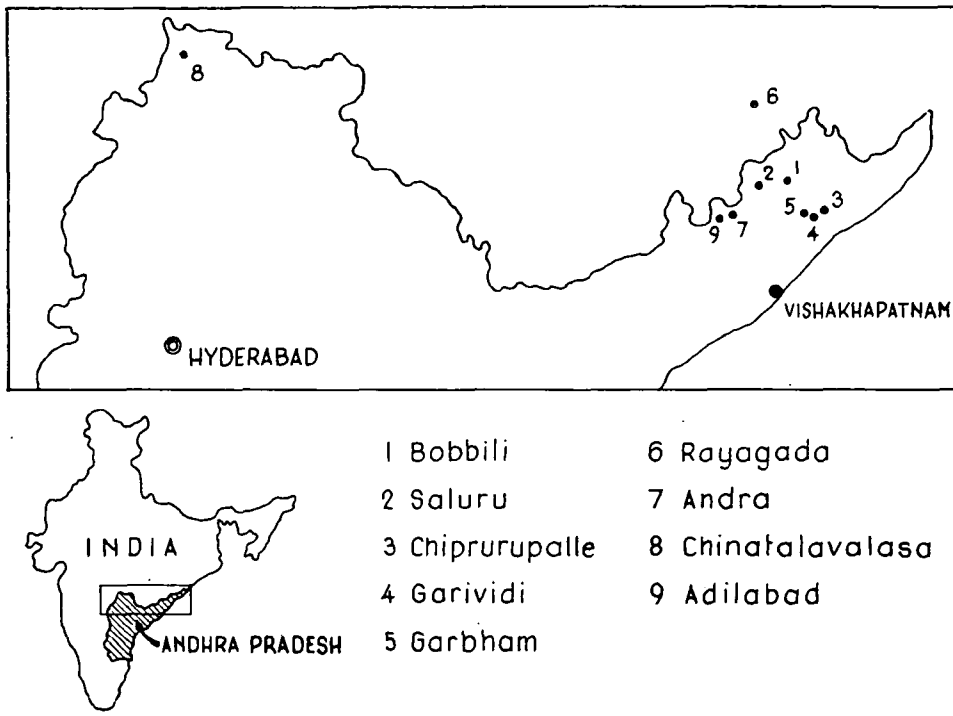

Fig. 1.

Some important structures of primary and secondary ores are given below:

1) At Garbham the manganese ores occur as conformable beds with quartzites with or without garnets. The manganese beds on average are 25 feet in thickness and show thickening due to folding. There is faulting also associated with chert formation, development of slicken slides, lithomarge, fault gouse, chlorite and epidote mineralisation.

2) At Koduru manganese beds occur discontinuously showing folds but appear as local pockets due to much disturbance. Weathering of the manganese bands, particularly by circulating waters concentrate secondary ores in the oxidation zone, extending to a depth of 75 to 100 feet. The manganese ores and associated rocks are metamorphosed and hence the recognition of their original features is difficult. Added to this, a step-like faulting in E—W direction is probable in Koduru area and hence in places like Devada, Duvvam, Sadanandapuram and Chipurupalle the deposits are of different thickness, width and are complicated by chertification and lithomarge formation.

3) In Rayagada and Saluru-Bobbili areas, manganese ores occur along with the khondalites conformably as beds and are concentrated on the surface as secondary ores. The khondalites are lateritized but did not give rise to manganese ores by themselves except some of the garnets of the khondalites show alteration to manganese ores.

4) Calc-granulites overlie manganese ores in Koduru, Garividi, Nellimarla areas. The manganese ores and calc-granulites form conformable bands and are surrounded by huge mass of granite gneiss with or without garnets in them. As in

Koduru the khondalites are enclosed in garnetiferous gneisses. At Taduru, Andra and Chintalavalasa the khondalites are conformable with manganese beds. Thus the khondalite series constitute quartzites with or without garnet; khondalites most of them devoid of graphite; calc-granulites mostly consisting of calc-silicates like diopside-hedenbergite series, anorthite, wollastonite, scapolite, garnet associate the primary manganese ores. The secondary manganese ores occur as powder up to a depth of 100 feet near Duvvam mine overlain by highly altered lithomarge, suggesting disintegration of manganese ores in situ.

Vizianagram Mining Company made some bore holes at Koduru where compact to friable ores are observable in logs, the ores are extending beyond a depth of 150 feet and are overlain by the khondalites. Alteration due to oxidation and formation of secondary ores is prevalent in the zone of meteoric waters up to 100 feet. It is important to note that these bore holes do not have any rock type similar to the so called '*kodurite*'.

At Adilabad manganese ores occur in association with limestones which are least metamorphosed. The ore bands associated with jasper bands which are a few centimeters in thickness. The layered nature of these ores is similar to a banded hematite quartzites in Bihar. Also some layering is found between silica and manganese ores observed in other places of Andhra Pradesh like Gotnandi, Yettacherla [KRISHNA RAO, 1955]. Perhaps this represents the original gel like formation of manganese oxide and silica in Precambrian rocks.

ASSOCIATION AND FIELD RELATIONS

Chipurupalle

The khondalites which form the country rock of the area have a wide distribution, and most of the hills are composed of it. These occur as low lying hills covered by laterite soils on sides. The khondalites show a general strike direction N 45° E and dip is varying about 45°—75° S.

Quartzites in the southern part of Chipurupalle area, occur in close association with khondalites showing the same strike direction and also dip as those of the khondalites.

Calc-granulites are few being confined to one patch at Chipurupalle over a width of about 10 feet striking N—E, another at Gadabavalasa distributed for a length of 60 feet striking N 35° E and dipping at 50° S and another at Viziarampuram south of Chipurupalle over a width of 4 to 5 feet.

Granites occur all around Chipurupalle. These are small mounds and, occur typical at Gollalapeta, Kottapeta, Muchinivalasa and Jada. Towards the north of the area Maradubaka, Jaggayyapeta, Aguru, Terlam and Panukuvalasa, an inequigranular variety of granitic gneisses are observed. The granites in the above places are more prominant than south of Chipurupalle where these are equigranular. Quartz, felspar, muscovite veins and quartz veins occur at a number of places cutting along the khondalites.

Manganese rocks — the so called '*kodurite*' of FERMOR which according to him are exposed in manganese mines are not found in these places. The various manganese pits observed show ores of all grades and the ore occurs mostly in the oxide form, pyrolusite and psilomelane. Pyrolusite is more abundant than psilomelane. Braunite in crystalline form occurs in Bondapalle. The pits are shallow and the important pits are Garraju Chipurupalle, Avagudem and Perumali, and they are

worked to a depth of 100 feet. At various places kaolin, chert and silica are seen. These are secondary products associated with the ore and their amount is not always the same as seen in the various pits of manganese.

Garividi and Garbham

The khondalite hill north of the Garbham pit is traversed by quartz-felspar veins at the contact of which large flakes of graphite have developed. Graphite has been prospected in this area as is evidenced by the presence of several small shallow trail pits. In the hill south of the Garbham pit the sillimanite gneisses at the base are succeeded by coarse grained quartzites on top with a bed of manganese ore about one foot in thickness sandwitched at the junction of the two.

The quartzites maintain the same strike as the underlying khondalites dipping 62° SW.

Cherts are very common and have small shining crystals of the garnet in them. Generally the garnets show alteration. The cherts are traversed by several small ramifying veins and stringers of white secondary silica. These appear to be latter than the actual masses of chert which enclose them. At Garbham south side of the main pit, huge irregular masses of chert are found. These cherts are exposed during the mining operations and are found to pass imperceptibly into kaolin.

Andra

Khondalites occur striking N 70° E and dipping 65° in SE direction. In south east corner of the area the strike changes to N 125° E and the dip is 70° SW.

Garnetiferous-biotite gneisses strike N 70° E and dip 65° SE direction at Kondagudavalsa. But in the south east corner of the area, the strikeis N 125° E and dip is 70° in SW direction. Some of these gneisses have concentration of felspars in them.

Khondalites occur and strike N 70° E and dip 65° SE. Further in the southern mid half of the area, the rocks strike N 125° E and dip 70° in SW direction.

Quartzites are sometimes banded containing garnets and graphite occur in the area, and exhibiting varying strike and dip.

Calc-granulites and calciphyres are also found as bands near about the adjoining area.

Manganiferous rocks occur in manganese pits of Garuguvalasa. The manganese band is traced over a distance of 350 feet striking N 70° E and dipping 65° in SE direction. The thickness of the band is 10 feet. The manganese band also consists of manganese pyroxenes and garnets.

Saluru — Bobbili area

The general strike of the rock formations consisting of khondalite series veers from N. N. W.—S. S. E in the west to N. N. E—S. S.E in the east and the dip is generally high (60°—70°) with a corrosponding swing from E.N.E to E. S.E.

Rayagada

The important rock formations are khondalites and charnockites occur in a dreary repetition, with general strike N.E—S.W to N.N.E and S.S.W.

Khondalites show a general N.N.E direction though the strike varies N.E and S.W locally. The dip varies from 50° to 70° E. Manganese ore occurs in close asso-

ciation with the khondalites. The persistance of the same strike for the manganese deposits and their occurrence all along the strike and gradation into garnetiferous gneisses and quartzites suggest that the magnanese bands are formerly sedimentary later metamorphosed like the other para-gneisses in the area.

The close association of garnetiferous gneisses and quartzites is an indication of the sequence in the deposition of sediments. They contain garnest, biotite, graphite, sillimanite and apatite as accessories.

Calc-granulites occur between Karli and Miragai over a distance of nearly 2 miles. The strike is N 25° E and the amount of dip is 50°. The calc-granulites are devoid of any manganese ores.

GEOCHEMISTRY

Manganese ores are variable in their manganese content at various places. But when compared to Madhya Pradesh the ores are lower in grade ranging anything from 22% to 45% rarely 48% to 50%. The phosphorous content is distinctly high in these ores and ranges from 0,1 lowest to 0.3 and sometimes 0,4 to 0,5. The average phosphorous content can be 0,15 to 0.25 in most of these ores. As the phosphorous is high the ores are not in demand and blending with low phosphorous bearing ores necessary to market them. Many Ferroy Alloy Plants were so designed that the phosphorous content of the ores is deliterious and hence methods for removal of phosphorous have to be adopted. The iron content and aluminium content also show variation. The following table shows some elemental distribution at various places.

Constituents	Chipurupalle	Garividi Garbham	Duvvam	Andra	Adilabad	Rayagada
MnO	3.70	2.27	0.09	0.50	0.50	0.99
Al_2O_3	20.64	17.30	12.49	9.65	5.00	19.66
Fe_2O_3	0.86	1.20	3.76	2.68	1.00	2.67
FeO	1.12	8.04	6.70	5.03	—	5.04
P_2O_5	1.01	0.75	—	0.18	—	0.39
SiO_2	68.38	58.04	70.16	74.35	19.22	74.38

The manganese ores consist of primary and secondary minerals particularly those from the oxidation zone. The following minerals are identified by ore microscope and confirmed by *X*-ray methods.

Name of the *mineral*	Garividi	Koduru mines	Adilabad	Rayagada	Andra	Garbham
Pyrolusite	+	+	+		+	+
Psilomelane	+	+	+		+	+
Vredenburgite	+	+				+
Braunite	+		+			+
Bixbyite	+					
Lithiophorite	+					
Franklinite		+				
Rhodonite	+	+			+	
Mn-garnet	+	+			+	
Coulsonite		+				
Hausmannite	+	+	+			+
Jacobsite	+	+			+	+

+ Present

The mineralogy of manganese ores is distinct in that it has no representation of carbonates or sulphides. It may be also noted that the mineral apatite in some of these ores or associated rock formations did not contain manganese in their constitution.

Texturally the primary ores exhibit gneissic foliation, the granularity being medium. The mineral vredenburgite is well known consisting of hausmannite-jacobsite intergrowth. Braunite is subhedral, associating with jacobsite and shows boron content in it [KRISHNA RAO, 1956]. The jacobsite is shown to be a solid solution series with magnetite [SUPRIYA ROY, 1959]. The coulsonite and franklinite are described by KRISHNA RAO. Pyrolusite is common in lamellar and granular form. Garnet, rhodonite and bustamite are the silicates. The mineral aggregates are recrystallized.

The secondary minerals are psilomelane varieties with barium and other elements like Co, Ni, etc. The secondary ores associate with silica, jasper bands and consist of various amounts of H_2O, limonite, goethite. The ores show botryoidal, stalactitic, sometimes stalagmitic and concretionary appearance, of various sizes. The secondary minerals also occur in joints and cracks.

The distribution of manganese content in various rocks in the area is as follows:

Rock	Koduru	Raya-gada	Saluru Bobbili	Andra	Chipuru-palle	Garbham
Khondalite		0.99		0.99	3.70	2.27
Granite		0.78	0.23	0.03		tr
Calc-granulite	3.36	0.33	0.31		2.37	0.14
Quartzites		1.05				
Garnets				24.46	0.25	12.72

The rocks and minerals with or without manganese deposits in the area do not show trends of variation of manganese content that could be correlate with magmatic process. It is also to be stated that some of the granites like that of Chipurupalle are paragneisses and not magmatic. The contact of various rocks in the area do not show manganese enrichment or segregation of manganese bearing minerals. The distribution of manganese is essentially an original constituent formed by the same geochemical process as the rocks and minerals in the area. Many of rocks in the manganese bearing areas have been shown to belong to khondalite series considered as paragneisses.

The following Table shows the mineral assemblages characteristic of upper amphibolite — granulite facies, found in association with manganese ores:

		Chipurupalle	
Khondalites	*Calc-granulites*	*Quartzites*	*Kodurites*
Quartz	Diopside	Quartz	Quartz
Garnet	Scapolite	Garnet	Felspar
Sillimanite	Wollastonite	Apatite	Garnet
Felspar	Felspar		Apatite
Apatite	Calcite		Biotite
Magnetite	Sphene		
	Apatite		

Garividi and Garbham

Garnet-sillimanite gneiss (Khondalite)	*Calc-granulites*	*Charnockites*	*Granite-gneisses*
Garnet	Diopside	Hypersthene	Felspar
Sillimanite	Wollastonite	Hornblende	Quartz
Felspar	Scapolite	Biotite	Garnet
Quartz	Apatite	Felspar	Biotite
Apatite	Felspar	Quartz	Apatite
Magnetite	Sphene		Magnetite
Sphene	Quartz		Sphene
Graphite	Calcite		
Biotite			

Andra

Khondalites	*Calc-silicate-rocks*	*Charnockites*	*Interaction rocks*
Quartz	Diopside	Diopside	Quartz
Felspar	Felspar	Hornblende	Orthoclase
Garnet	Quartz	Hypersthene	Plagioclase
Sillimanite	Plagioclase	Plagioclase	Garnet
Biotite	Sphene	Magnetite	Biotite
Magnetite	Wollastonite	Ilmenite	Hornblende
Graphite		Apatite	Hypersthene
Apatite			Zircon
Rutile			Ilmenite
Chlorite			
Zircon			

Saluru—Bobbili

Khondalites	*Calc-silicate-rocks*	*Charnockites*
Quartz	Diopside	Hypersthene
Felspar	Plagioclase	Biotite
Garnet	Feldspar	Garnet
Sillimanite	Quartz	Felspar
Graphite	Sphene	Quartz
Apatite	Wollastonite	Norite
Magnetite	Scapolite	
Rutile	Enstatite	
Biotite	Zoisite	
Cordierite	Sapphirine	
Spinel	Calcite	
Talc	Garnet	

Rayagada

Khondalites	*Calc-granulites*	*Quartzites*
Quartz	Diopside	Quartz
Sillimanite	Calcite	Garnet
Garnet	Wollastonite	Biotite
Felspar	Sphene	
Apatite	Feldspar	
Magnetite	Apatite	
	Quartz	

The manganiferous beds have been deposited as oxides pure to impure in nature and are recrystallized forming braunite, vredenburgite, pyrolusite, pyroxene and granulite assemblages, sometimes with relict primary sedimentary features. Therefore it is surmised that there should have been peculiar geochemical conditions in the formation of manganese oxides during Precambrian in India. It is also possible that some biogenic process may be operating at some stages as in Adilabad where fossil imprints of very primitive nature were observed.

The geochemistry has an important unique problem namely the association of high phosphorous in the ores unlike in many other parts of manganese deposits of India. Apatite could be a source for high phosphorous and it is found as granular, needle like, platy [KRISHNA RAO, 1966] or as crystals through which cavities are made and secondary manganese solutions are circulated. The apatite is present in accessory amounts in granitic gneisses, calc-granulites to certain extent and rarely with manganese bearing bands. Such apatite occurring free in ores can be separated by mechanical methods. But the phosphorous content is not fully due to this type of associated with iron content of manganese ores. It is stated by the mine owners in these area that phosphorous increases with depth. However, it is observed [KRISHNA RAO, 1956] that bore hole samples of manganese ores at depth are relatively poor in phosphorous. It is also observed that phosphorous distribution is not following any regularity either area wise or ore wise or depth wise. Thus the problem of high phosphorous has to be sorted out yet, and the phosphorous is to be located carefully befor this undesirable element is removed for better use and market of the ores.

CONCLUSIONS

The above account on structure, ore petrology and geochemistry of manganese ores of Andhra Pradesh throws open very interesting and challenging problems. The ores needed to be located in interior Eastern Ghats where these may be more amenable for geological prospecting by structural mapping of major as well as minor structures. The primary ore band consisting of oxides, sometimes silicates is confirmable with the khondalite series (with one of the members) which show drag folding locally.

The secondary ores formed in fault zones both major and minor. The mineral assemblages observable in reflected light with the aid of *X*-ray confirmation can again be sorted out into primary and secondary, the latter being called as '*wad*' usually. The mineralogy and textures give an important information on geochemical evolution of the ores since their formation.

The structure and mineralogy of the ores and distribution of elements like P, Ni, Cr, Co should be examined and geochemical process studied so that the ores can be categorized for special use and to carry out experiments to eliminate deleterious elements for a better use of these ores.

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CO-AXIAL QUARTZ TWIN CRYSTALS WITH RADIATE CONCRESCENCE IN THE DEPOSIT OCNA-DE-FIER, BANAT, RUMANIA

CONSTANTIN GRUESCU

In the paper a new sort of quartz twin crystal is reported, which has been recently discovered in the Reichenstein body of the mineralized complex of the classical iron deposit Ocna-de-Fier (Banat, Rumania).

The classical contact deposit at Ocna-de-Fier has been known from ancient times. A more detailed description has been given in the XVIIIth century by C. DELIUS [1738], I. V. BORN [1774], afterwards B. V. COTTA [1864] and later AL. CODARCEA [1931], A. KISSLING [1967] and SERBAN VLAD [1974].

The deposit is located on the geotectonical alignment bearing of Western-Banat, in the contact zones of the Mesozoic geosyncline Ocna-de-Fier — Calina with the Banat magmatites.

The complex mineralization of the deposit is composed of more than 100 ores and scarn minerals some of which — e.g. the ludwigite and the dognacskaite as well as others — are famous throughout the world. They have been described and located for the first time in this deposit.

Quartz is of major importance among the minerals quoted, including the catathermal Japanese twin crystals and the recently identified twin crystals to be described in this paper.

During the mining operations of the deposit in the Reichenstein I—heading, Delius-zone of the Ocna-de-Fier mine, a geode was found including several quartz crystal aggregations of unusual shape.

The geode is located in the upper zone of the deposit, at the boundary between crystalline limestone and garnetiferous scarns, about 3 m/150 m in size, with North-South orientation the crystalline limestone in the Western wall of the geode is granoblastic, grain size up to 1.5 mm.

The scarn in the Eastern wall of the geode is granular, massive; due to the garnet of the grossularite = andradite series its colour is generally yellowish-brown. In some places greyish-green spots are noted, consisting of short prisms up to 0.5 cm in length, sometimes in divergent arrangement; most probably it is a diopside partially passing to tremolite.

In more distant locations of the geode, the scarn consists of a mineralization composed of magnetite in shape of strips of millimetre thickness alternating with scarn strips.

To note that the geode is lined mainly with well developed crystals representing a quartz pseudomorph after apatite, pyroxene and less calcite *(Fig. 1)*.

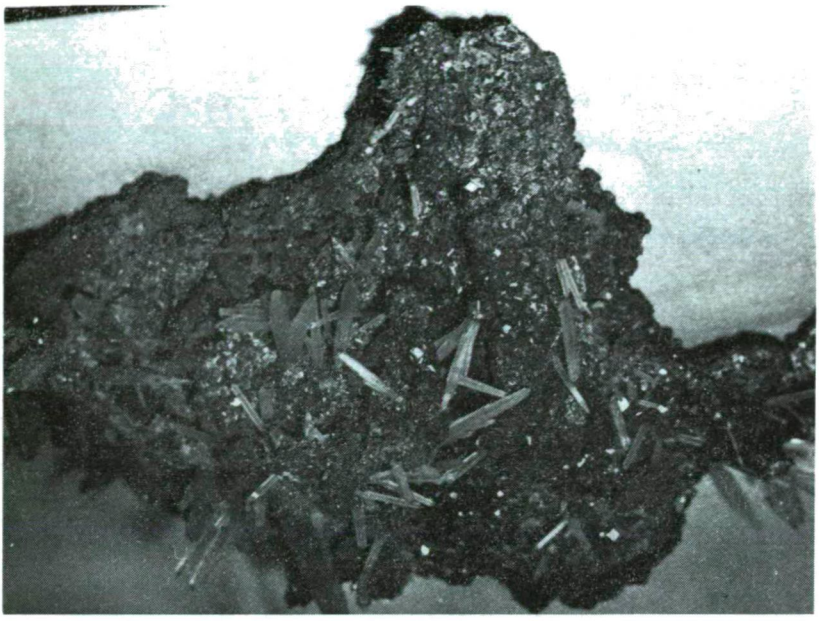

Fig. 1. Well-developed quartz crystals pseudomorph after apatite, pyroxene and less calcite. Natural size.

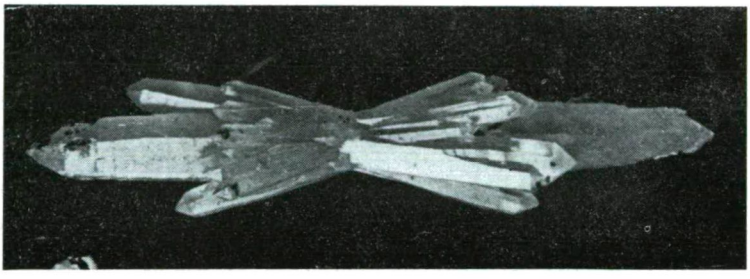

Fig. 2. Interpenetration of two co-axial quartz twin crystals, the angle amounts to 43°. Natural size.

In addition to quartz crystallized in shape of the white and translucid pneudomorphs cited, another series of well developed quartz crystals occurs in lesser amounts and of more transparent appearance; the garnet crystals are rhombicdodecahedrons as well as in lesser amount, trapezohedrons.

The crystals are situated on a limonitic hematite crust up to 0.8 cm in thickness.

The centre of the geode was filled with a reddishbrown clayey material. In this plastic mass perfectly developed quartz crystals were found. A number of these, of small size, were attached to more or less undulating platelets composed of idiomorphous crystals nearly equal in size, amounting in the main to 3—4 mm. Other quartz crystals were found perfectly developed in the clayey mass.

The particular novelty to be reported, especially with unfixated crystals, has been the existence of a "co-axial quartz twin crystal with radiate concrescences".

Three different types of twins can be distinguished by starting from the simple to the complex:

1) A co-axial twin crystal where the individuals of smaller size — 2—4 cm — show radiate twinning about a single individual, the axis of symmetry A.6, the length of which much exceeds that of the other individuals in radiate arrangement and making a 20° angle *(Fig. 2)*.

2) Interpenetration of a couple of co-axial twin crystals, the angle subtended by interpenetration amounting to 43° *(Fig. 3)*.

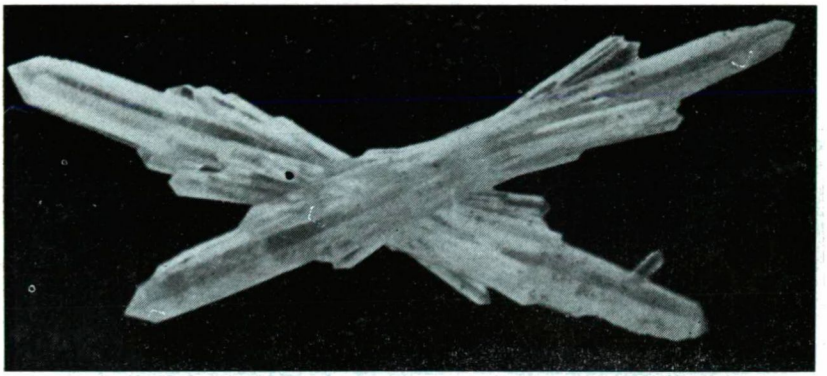

Fig. 3. Twin consisting of three individuals. Natural size.

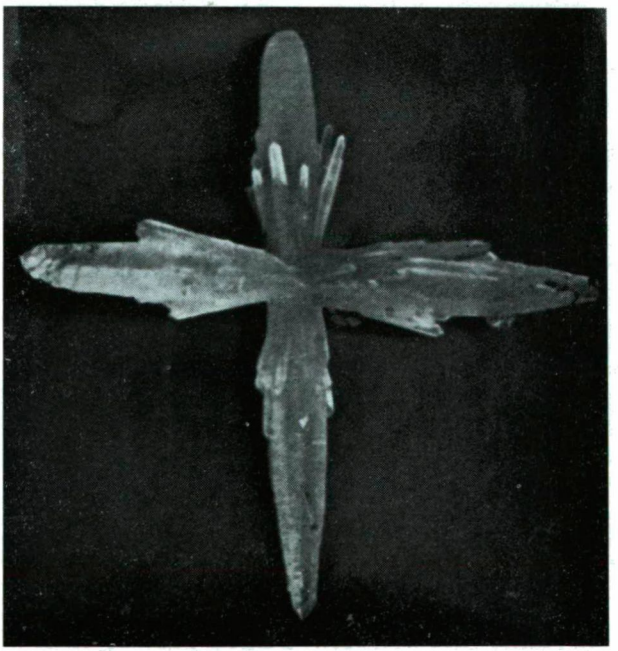

Fig. 4. Quartz twin crystals. 2/3 natural size.

3) Twinning of three individuals as follows:

On one hand, twinning of each of the individuals is coaxial and radiate. Two of the individuals, of more elongated shape, interpenetrate by subtending a 90° angle, while the plane they subtend, interpenetrates with the third individual making a 20° angle.

On the whole, the above described triple twinning is in shape of a cross with nearly equal arms *(Fig. 4)*.

To note that the 20° angle of twinning, in case of the third kind of twinning described, is equal to the 20° angle of co-axial twinning with radiate concrescence.

Of the crystal faces, the prism $10\bar{1}0$ faces are best developed on all individuals.

To note that onto some of the quartz crystals, black calcite crystals are grafted, the faces of which are striated; the size of the trigonal scalenohedrons of calcite crystals varies between 1 to 13 cm *(Fig. 5)*.

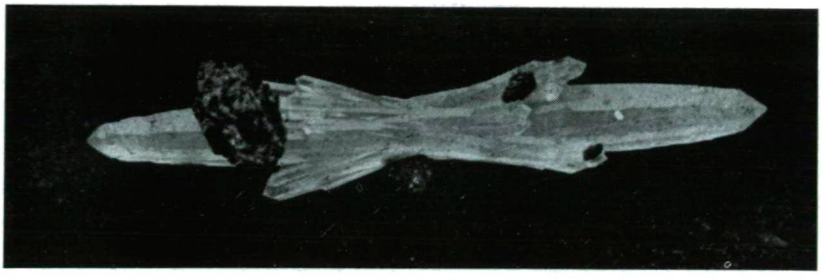

Fig. 5. Quartz twin. Natural size.

The quartz crystals are nearly transparent.

The paper is the first in Rumania to report identification of a new kind of co-axial twinning discovered by the author in the Reichenstein body of the classical contact deposit at Ocna-de-Fier in Banat.

The twin crystal type described is characterized by co-axial twinning according to the A6-axis of the bigger individuals, while the smaller individuals are radially arranged to the first, subtending an angle of 20°.

There are cases of interpenetration of 2 or 3 individuals with co-axial mode of twinning; however, in those cases too, crystals of smaller size in radiate arrangement are found.

The crystallographic measurements have been carried out in the Institute for Oil, Gas and Technical Geology, Bucharest, by PROFFESSOR ANA MERCUS.

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SINTERING OF ROSETTA ZIRCON WITH CALCITE

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ABSTRACT

Sintering of zircon with calcium carbonate or oxide was reported to take place completely at temperature range 1400—1500 °C.

This work represents a thermal investigation of sintering of Rosetta zircon with calcite in presence of graphite by using derivatograph. The products of sintering were identified by using a Siemens crystalloflex diffractometer. The process of sintering results in the formation of calcium zirconate $CaZrO_3$ and calcium silicate of composition $3\ CaO \cdot SiO_2$.

INTRODUCTION

Among the minerals of the black sand of Egypt is zircon which is found in an economic amount (7.29%). These sands are found along the Mediterranean coast of Nile Delta. These sands are enriched by gravity concentration methods followed by magnetic and electrostatic separation [ABDEL REHIM, 1974 and ANWAR *et al.*, 1970].

There are different methods of chemical processing of zircon to obtain zirconium oxide [ANWAR *et al.*, 1970; MIRSON *et al.*, 1965 and ZELIKMAN *et al.*, 1964]. These include sintering of zircon with soda, alkali or calcium oxide and hydrometallurgical leaching with alkali solutions. Sintering of zircon with calcium oxide takes place only at 1400—1500 °C. Addition of some components such as $CaCl_2$ and CaF_2 leads to the decrease of temperature of the process [GALKIN *et al.*, 1971; MIRSON *et al.*, 1965 and ZELIKMAN *et al.*, 1964].

Non metamict zircon did not give any thermal reaction. Several data from literatures can be found on the thermal investigations of zircon, calcite and other calcium silicates [EYSEL *et al.*, 1974; FRONDEL, 1953; GALKIN *et al.*, 1971; GARRELS *et al.*, 1960; IVANOVA, 1961; KONDRASHOVA *et al.*, 1952; MACKENZIE, 1964 & 1962.] The thermogram of calcite shows a strong endothermic peak at 880 °C which represents its dissociation to calcium oxide and the liberation of carbon dioxide.

Little is known about the thermal character of reaction of sintering of zircon with calcium carbonate. This work represents a thermal investigation of sintering of Rosetta zircon with calcite in presence of graphite at considerably lower temperature than the temperature range reported earlier by using a derivatograph. Also, it includes a study of the products of sintering by *X*-ray powder diffraction analysis.

EXPERIMENTAL WORK

This work was carried out with zircon, separated from Egyptian black sand. Its chemical, mineralogical and *X*-ray analysis are given in Tables 1, 2 and 3, respectively. The *X*-ray powder data of calcite used in the mix are given in Table 4.

TABLE 1

Chemical composition of zircon concentrate

Chemical components	Content, %
SiO_2	32.40
ZrO_2	64.21
TiO_2	0.73
Fe_2O_3	1.57
Al_2O_3	0.68

TABLE 2

Mineralogical analysis of zircon concentrate

Mineral	Content, %
Zircon	96.70
Rutile	0.45
Ilmenite	0.68
Monazite	0.20
Epidote	0.53
Garnet	0.76
Amphiboles	0.10

TABLE 3

X-ray powder diffraction data of zircon

d(Å) ASTM	*d*(Å) Observed	*I* ASTM	*I* Observed	*hkl*
4.434	4.438	45	65	101
3.302	3.304	100	100	200
2.650	2.653	7	12	211
2.518	2.520	45	65	112
2.336	2.338	10	25	220
2.217	2.223	8	12	202
2.066	2.068	20	45	301
1.908	1.911	14	12	103
1.751	1.752	11	20	321
1.712	1.712	40	60	312
1.651	1.652	14	40	400
1.547	1.548	4	4	411
1.495	1.498	3	2	004
1.477	1.478	8	20	420

As shown from Table 2, contaminants include some ilmenite, rutile, monazite, garnet, amphibole and others in fine grains and in small amounts. Non of the contaminants was detected by *X*-ray analysis, therefore, no individual mineral may be present as a major constituent which is in consistence with the mineralogical data. The total ZrO_2 content in pure zircon should be 67.22%.

TABLE 4

X-ray powder diffraction data of calcite

d(Å) ASTM	*d*(Å) Observed	*I* ASTM	*I* Observed	*hkl*
3.86	3.850	12	12	102
3.035	3.035	100	100	104
2.845	2.840	3	3	006
2.495	2.498	14	16	110
2.285	2.284	18	22	113
2.095	2.095	18	18	202
1.927	1.926	5	6	204
1.913	1.913	17	17	108
1.875	1.875	17	22	116
1.626	1.626	4	4	211
1.604	1.604	8	10	212
1.587	1.586	2	2	1.0.10
1.525	1.524	5	6	214
1.518	1.521	4	4	208
1.510	1.509	3	2	119
1.473	1.472	2	2	215
1.440	1.438	5	6	300
1.422	1.434	3	3	0.0.12

TECHNIQUES OF WORK

Starting materials

Starting materials usually consisted of zircon mixes. Reagents used in mixes are calcite and graphite in particular amounts. Mixes were processed by repeated grinding in an automated agate mortar and sieving till all the powder pass through 200 mesh sieve and pestle for one hour to achieve homogeneity.

Sample container and apparatus

Sintering runs were carried out in ceramic crucibles, heated in an electrical furnace. The character of the reactions of sintering of zircon with calcite in presence of graphite was studied by thermal analysis using F. PAULIK, J. PAULIK and L. ERDEY derivatograph [PAULIK *et al.*, 1966].

This apparatus records simultaneously four thermal curves: (T).the change of temperature of the sample, (DTA) differential thermal analysis, (TG) thermogravimetric (quantitatively in mg) and (DTG) derivative thermogravimetric, on a single sample under controlled conditions. DTA and temperature measuring thermocouples are Pt/Pt-Rh wires. Ceramic crucible and a ceramic sample holder were used. Alumina, calcined at 1000 °C, was used as a reference material. The parameters during tests were as follows: Weight of sample 1 gm, T — 1200, DTA — 1/10, DTG — 1/10, TG — 500 mg and heating rate of 10 °C per minute. All determinations were carried out in air atmosphere under suction of carbon dioxide.

Phase identification and characterization

The end products of zircon sintering with calcite were studied both microscopically and by *X*-ray analysis.

X-ray Procedure

A Siemens Crystalloflex diffractometer was used with nickel filtered copper radiation. Exposure was one hour and scanning speed was 1° 2Θ per minute at 1 cm per minute chart speed. Intensities were collected to maximum $2\Theta = 65°$. The sensitivity of the experiment was 1×10^4 impl./min., and the statistical error was 1.5%.

Chemical analysis of the end product of sintering was carried out for the determination of the efficiency of sintering. Before studying the thermal character of the reaction of sintering of zircon with calcite, a calculation of its thermodynamic constants was estimated. The standard free energy ($F°$) and the equilibrium constant (K) of the reaction were -20.60 Kcal/mol and 1.29×10^{15}, respectively.

RESULTS AND DISCUSSION

The derivatogram of zircon mixture with calcite of amount 15% of theoretical value and graphite in the suitable amount 15% of zircon charge is shown in *Fig. 1.* The evaluation of the DTA curve of zircon mixture is based on its comparison with that of calcite and other components of the mix. The first small endothermic peak at

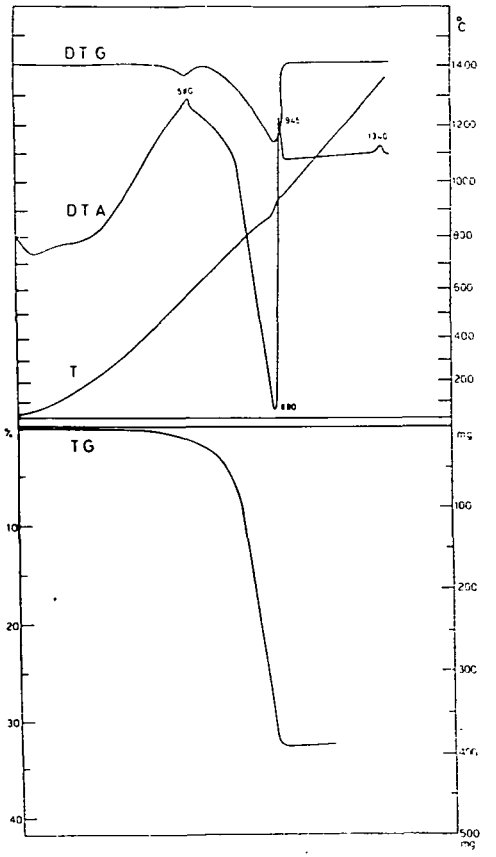

Fig. 1. Derivatogram of zircon sintering with calcite in presence of graphite. Weight of sample 1000 mg. Heating rate 10 °C/min.

70 °C represents the dehydration of the mix. The sharp exothermic peak at 580 °C may be due to the burning of graphite and the combustion of volatiles. This is accompanied by some decrease in weight (TG). The large endothermic peak at 880 °C, represents the intensive dissociation of calcite and the reaction between zircon and the resultant calcium oxide. This process is connected with a remarkable decrease in weight (TG) due to the liberation of carbon dioxide. According to the thermal curve of this mixture, the beginning of sintering and decomposition of calcite follows directly the end of the exothermic reaction.

The exothermic peak at 945 °C may be connected with the reaction between zircon and calcium oxide and probably transition of the resulted calcium silicate to another form. The transition temperature is previously recorded near to this value [EYSE *et al.*, 1974].

There is a small exothermic peak at 1340 °C which is under study and probably due to the congruent melting of resulted sphene, since the temperature of melting of sphene was recorded as 1382 °C.

The *X*-ray powder diffraction pattern shows the first appearance of calcium zirconate and silicate above 700 °C as shown in figures 2 and 3.

The sintering process results in the formation of calcium zirconate and calcium silicate of composition $3CaO \cdot SiO_2$ instead of $CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ as recorded previously [MIRSON *et al.*, 1965 and ZELIKMAN *et al*, 1964]. Their *X*-ray powder diffraction data are given in Tables 5 & 6. The obtained calcium zirconate will be directed for dissolution process using hydrochloric or sulphuric acid for extraction of zirconium.

For studying the effect of temperature on sintering of zircon, some runs were carried out using zircon mixes with calcite and graphite in amount 15% of zircon charge, at temperature ranging from 850 °C up to 1050 °C during 5 hours.

From the obtained results (Table 7), it is shown that the sintering efficiency of zircon sharply increases with temperature. It is observed that nearly complete sin-

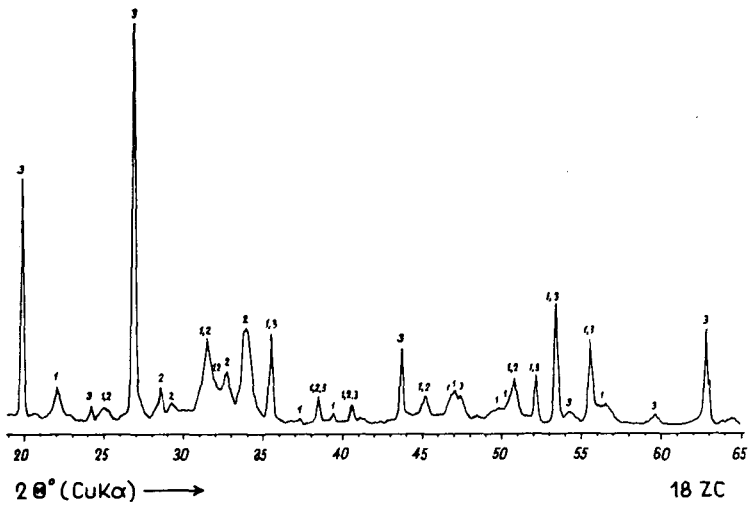

Fig. 2. *X*-ray powder diffraction pattern of the products of zircon sintering at 700 °C
1 — Calcium zirconate
2 — Calcium silicate
3 — Zircon

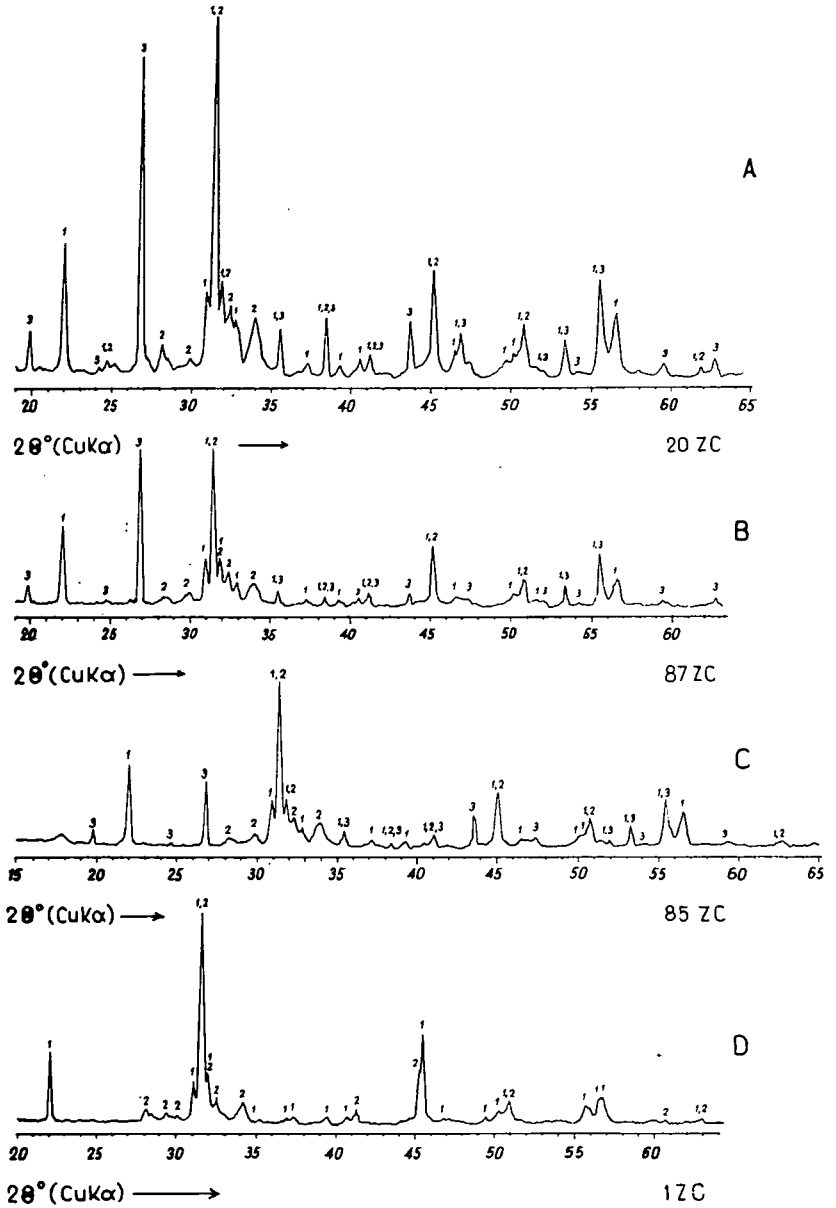

Fig. 3. *X*-ray powder diffraction pattern of the products of zircon sintering with calcite in presence of graphite (A), (B), (C) and (D) at 850, 900, 950 and 1050 °C.
1 — Calcium zirconate
2 — Calcium silicate
3 — Zircon

TABLE 5

X-ray powder diffraction data of calcium zirconate

d(Å) ASTM	*d*(Å) Observed	*I* ASTM	*I* Observed	*hkl*
4.01	4.006	80	90	200, 020
3.58	3.587	40	20	120, 210
2.87	2.872	80	60	$\bar{2}02$
2.83	2.836	100	100	220, 022
2.79	2.794	80	68	202
2.70	2.714	10	28	$\bar{2}12$
2.55	2.547	10	28	$\bar{1}03$, $\bar{3}01$
2.51	2.513	40	25	103, 301
2.43	2.430	40	25	$\bar{1}13$, $\bar{3}11$
2.41	2.409	40	25	131
2.39	2.400	40	25	113, 311
2.33	2.338	20	22	$\bar{2}22$
2.29	2.287	20	111	222
2.22	2.219	40	20	023, $\bar{3}21$
2.13	2.128	10	9	132, 231
2.00	2.002	100	90	400, 040
1.957	1.945	20	22	401, 104
1.939	1.932	40	36	014, 041
1.845	1.839	10	14	$\bar{1}33$, $\bar{3}31$
1.828	1.829	10	13	133, 331
1.811	1.812	40	20	$\bar{2}04$, $\bar{4}02$
1.789	1.792	60	50	024, 042
1,751	1.753	10	9	$\bar{1}42$, $\bar{2}41$
1.727	1.713	10	9	214, 412
1.651	1.651	80	78	$\bar{2}24$, $\bar{4}22$
1.642	1.643	6	6	$\bar{2}42$
1.625	1.628	60	40	242
1.617	1.624	80	50	224, 422
1.498	1.499	40	15	$\bar{2}34$, $\bar{4}32$

tering of zircon (96.6%) takes place at 1050 °C. The products of sintering of these runs were identified microscopically and by *X*-ray diffractometer. By microscopic examination of thin sections of the products of sintering at 850, 900, 950 °C, it is observed that considerable numbers of zircon grains were detected in the runs at 850 and 900 °C. At 950 °C the amount of zircon grains decreases in the sintered product. This gives good idea about incomplete sintering. The product obtained in the run at 1050 °C consists mainly of calcium zirconate and silicate with few fine grains of zircon.

The *X*-ray powder diffraction patterns of these products of sintering at 850, 900, 950 and 1050 °C are shown in *Fig. 3*. Zircon is present in large amounts in the runs A, B and C and its peaks are completely disappeared in the product of run D at 1050 °C. It is observed that the X-ray peaks of zircon are less intense as the temperatures rises. The X-ray peaks of calcium zirconate and silicate are narrow and intense, suggesting good crystallinity.

The microscopic study of the product phases of zircon sintering with calcite is in good agreement with the X-ray powder diffraction patterns.

TABLE 6

X-ray powder diffraction data of calcium silicate ($3CaO \cdot SiO_2$)

d(Å) ASTM	d(Å) Observed	I ASTM	I Observed	*hkl*
3.07	3.090	90	40	201
3.01	3.020	30	15	202
2.84	2.838	70	80	009
2.787	2.794	100	100	204
2.739	2.744	6	10	116
2.649	2.639	100	70	205
2.362	2.365	20	12	207
2.331	2.338	6	7	211
2.303	2.310	4	4	212
2.224	2.220	50	30	119
2.198	2.189	16	22	214
2.006	2.004	12	40	303
1.971	1.986	18	50	210, 010
1.858	1.861	8	14	301
1.830	1.829	2	4	1.1.12
1.789	1.792	55	60	220
1.669	1.678	4	10	309
1.659	1.662	16	30	314
1.575	1.576	10	10	2.1.12
1.537	1.539	4	7	402
1.513	1.516	25	16	229, 318
1.505	1.510	6	6	404
1.482	1.478	12	10	405

TABLE 7

Effect of temperature on sintering efficiency of zircon

Temperature, °C	Sintering efficiency, %
850	56,8
900	67.3
950	83.7
1050	96.6

CONCLUSIONS

From the thermal investigation of sintering of Rosetta zircon with calcite of amount 15% in presence of graphite has revealed that nearly its complete sintering can be reached at 1050 °C. This temperature is distinctly lower than the temperature range reported earlier.

The microscopic and *X*-ray diffraction study shows that the sintering of zircon results in the formation of calcium metazirconate and calcium silicate of composition $CaZrO_3$ and $3CaO \cdot SiO_2$ respectively.

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COMPARISON BETWEEN THE X-RAY DIFFRACTOMETRIC QUANTITATIVE DETERMINATION METHODS OF CALCITE AND DOLOMITE ON THE BASIS OF THE INVESTIGATION OF NEOGENE SEDIMENTS OF THE GREAT PLAIN

J. MEZŐSI

INTRODUCTION

In the course of the investigation of the clastic sedimentary rocks the qualitative and quantitative determination of the carbonate ingredients being in most of the cases calcite and/or dolomite, is necessary.

The procedure is well-known from literature that in the *X*-ray diffractograms the quantitative ratio of calcite/dolomite can be determined on the basis of the ratio of most intense peaks of calcite and dolomite. This is advantageous mainly in the cases when the rock does not contain other main components. In case of 10 to 90 per cent dolomite content the determination is of ± 5 per cent accuracy by means of the calibration curve constructed by C. B. TENNANT and R. W. BERGER [1957].

Applying this method the absolute quantity of the clastic calcite/dolomite can also be determined when the CO_2-content has been previously determined. In this case taking into account the CO_2 quantity the quantities of calcite and dolomite can be computed by means of the calibration curve [J. C. VAN MOORT, 1973].

In case of deep-bore samples there is an ever increasing demand for the qualitative and quantitative determination of clay minerals, chlorites, carbonates, feldspars and quartz. In case of the *X*-ray diffractometric investigations the possibility of serial analyse is given and within smaller limits of error the quantities of these minerals can be determined from one diffractogram; thus without the CO_2 determination the quantities of calcite and dolomite are obtainable from one diffractogram. In this case when multiplying the intensity of the most characteristic peaks of the single crystalline phases with the corresponding constants, the intensity ratios will give quantitative ratios. In the present paper the calcite and dolomite quantities computed by this method from the diffractograms will be compared with the calcite and dolomite quantities obtained from the intensity ratio of the diffractograms and from the gasometrically determined CO_2 content.

DETERMINATION TECHNIQUES

The part of the core sample to be investigated, cleaned from drilling mud and of small faciological differences was crumbled down to pea-size than it was pulverized in ball and tube mill for 5 to 15 minutes depending on the quality of the material (clay, sandstone, etc.). Unfortunately, the required homogeneity could not be reached in all cases after grinding and this fact is responsible for the deviations between the methods. Inhomogeneity occurred mainly at those samples the marly part of which contained aleurite and sand strips often of mm-size. Both the *X*-ray record and the CO_2 determination were carried out from the average sample obtained in this way.

The latter one resulted in the CO_2 content of all the carbonates, since in these formations siderite and magnesite occurred only in negligible quantities, their determination was neglected and only the quantities of calcite and dolomite were determined.

It is well-known that in the diffractograms the size of the most intense reflexions of the single crystalline phases are to a certain extent proportional to their quantities in the mixtures (e.g. in clastic sedimentary rocks). The number of factors determining the intensity itself is highly depending on the structure's stability. Within the carbonate series the stability of the single phases is relatively high, consequently the coefficients used in the computations is rather similar in the literature. In case of these investigations the constants of 0.81 and 0.85 were used for the peaks of 3.03 Å of calcite resp. 2.88 Å of dolomite. It is obvious that not only the calcite and dolomite were identified in the diffractograms but all the phases amounting to more than 4 to 5 per cent were determined, while the amorphous phase was neglected since its quantity proved to be less than 5 per cent in most of the cases.

EVALUATION OF THE RESULTS

In the majority of the cases the calcite and dolomite quantity determined from the X-ray diffractograms was higher by 1 to 5 per cent than the directly computed calcite-dolomite values. In the samples of the bore Makó-2 the quantitative changes of calcite and dolomite determined by both methods are shown in Fig. *1*. It is apparent that the values concerning dolomite show good agreement, these are within the limit of error. The quantity computed from the *X*-ray diffractograms shows greater deviations in case of sandstones and aleurites which may be attributed to the late diagenetic dolomitization.

In case of calcite more considerable deviation was obtained in the clayey rocks. This is probably because of the slightly ordered illite and illite/montmorillonite structures of small reflexion and micron-size resulting in only shifts in proportions, further for the insufficient homogeneity of the samples from which the CO_2 determinations and *X*-ray diffractograms were recorded.

Similar phenomena were observed in the samples of Ferencszállás where mainly sandstones and aleurites were investigated, the marls and lime-marls were subordinate (Fig. *2*.). In these samples the sandstones showed positive deviation of 4 to 5 per cent in case of both calcite and dolomite while the lime-mud has given identical results. This latter fact was probably engendered by the accumulation of the sandy, resp., fine-sandy fraction at the expense of the clayey fraction.

The results obtained in the investigation of the Upper and Lower Pannonian formations of Endrőd show also good agreement, in general. In case of calcite deviation occurred when the carbonate phase was accompanied by considerable amount of clayey fraction, in the other samples the difference of data of the two methods did not exceed 4 to 6 per cent.

In case of dolomite slight deviation was observed in sandstones and aleurites, the other values show identical results.

H. FÜCHTBAUER and H. GOLDSCHMIDT determined the features which are characteristic of the early and late diagenesis. One of them is an important factor, *i.e.* the change of grain size. The grain size of the early diagenetic dolomites falls for the most part below 10 microns, while in case of late diagenesis when dolomitization followed only after the solidification of the sediment the grains are usually greater than 10 microns. Consequently, when treating the rock sample with H_2O_2 and having obtained the original grain size and separating the grain size fraction of less than

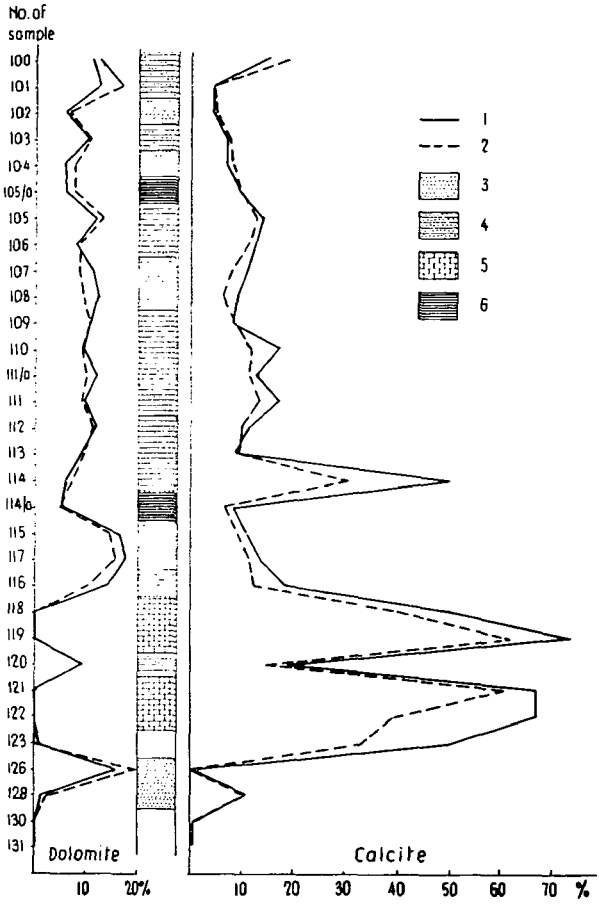

Fig. 1. Calcite and dolomite content in the samples from the bore Makó-2
Legend: *1)* The amount of calcite and dolomite, respectively, in per cent determined by x-ray diffractometry; *2)* Amount of calcite and dolomite, respectively, calculated on the basis of CO_2 content determined gasometrically; *3)* Sandstone; *4)* Aleurite; *5)* Lime-marl — limestone; *6)* Clay, clay marl.

10 microns, then in case of late diagenetic dolomite the quantity should decrease in this fraction. Results are summarized in Fig. *4*. It can be seen that in the fraction of less than 10 microns the dolomite quantity decreased as compared to the original average sample, and in certain cases this decrease amounted to 10 per cent, as well. This relates to the fact that dolomite is a late diagenetic mineral, in part at least, in these Neogene clastic formations.

The late diagenesis is characterized by the total absence of $CaSO_4$, and this typical also in these samples since neither anhydrite nor gypsum were found in these strata.

The formation of syngenetic dolomite should be taken into account to a certain extent which is proved by the fact that the lime-mud strata do not contain dolomite but show transition into dolomite-bearing strata within small distances. This pheno-

menon can be followed in the samples of Makó, Ferencszállás and Endrőd, as well. It can be said in general that where the quantity of calcite exceeds 50 per cent the dolomite is absent, and in such cases only minimal MgO was determined by the chemical analyses. This was probably resulted by the modification of the paleogeographic situation, or salinity has perhaps changed, to prove the latter statement, however, no exact data are available.

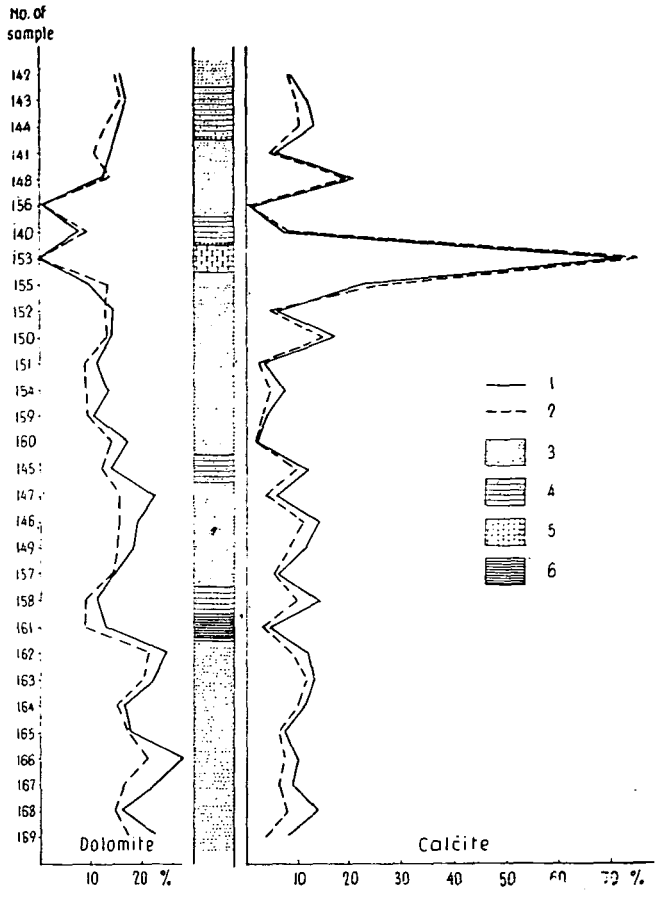

Fig. 2. Calcite and dolomite content of samples from the bore Ferencszállás (legend see *Fig. 1.*)

Dolomite is not always of stoichiometric composition and the experiences proved this in these samples. In case of increasing calcium surplus the orderedness of dolomite lattice decreases and the value of the d_{104} index is displaced towards the lower 2θ values. The built in of iron results in similar changes. Taking into consideration the changes of the d_{104} value of dolomite in the samples of Makó, Ferencszállás and Endrőd it can be stated that these values lye for the most part between 2.880 and 2.890 Å (Fig. 5.). In the bore of Makó the d_{104} value of dolomite of the clay-marl exceeds the 2.890 Å which corresponds to a composition of $Ca_{55}Mg_{45}$ (according to

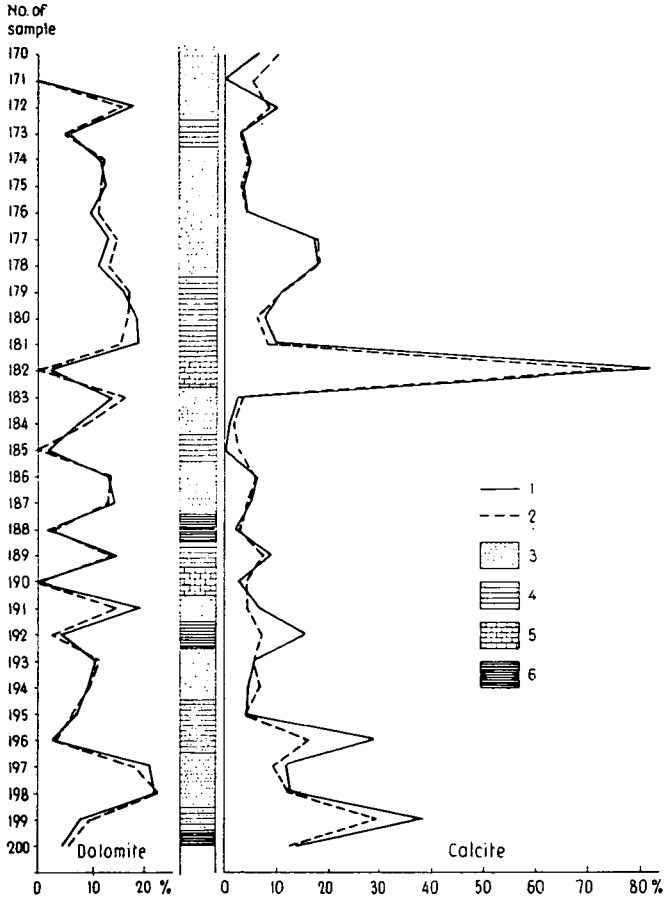

Fig. 3. Calcite and dolomite content of samples from the bore Endrőd (legend see *Fig. 1.*)

FÜCHTBAUER and GOLDSMIDT) this, however, equals to 46 mole per cent $MgCO_3$ after GOLDSCHMITH and GRAF. In the samples of Ferencszállás the values above 2.890 Å are absent. The $MgCO_3$ content varies between 47 and 49 per cent and hardly deviates from the stoichiometric composition. Out of the bores of Endrőd only below and above the Lower Pannonian lime-mud levels appears dolomite which was of a *d*-value higher than 2.890 Å and this equals to about 46 mole per cent $MgCO_3$ content. The other samples are nearly of stoichiometric composition. Consequently, in these samples it can be followed that when calcium ions are built in into the structure of dolomite, the d_{104} values are displaced towards that of calcite.

In some samples the d_{104} value of dolomite proved to be less than 2.880 Å. Taking into consideration the structural data and references of literature it should be assumed that the composition of dolomite was displaced towards magnesite. This is in accordance with the investigations of J. FR. SUREAU. As to his measurements the d_{104} value of dolomite etalon is 2.885 Å while that of the mineral of $Ca_{55}Mg_{45}$ com-

position is 2.897, in case of magnesitic dolomite 2.879 Å. All of these formations contained coalified plant remnants and proved to be sandstones or perhaps aleurites.

In our case protodolomite is out of question since it is a less ordered structure and does not occur in the Neogene clastic formations. The intensity relations of I 2,54/I 2,38 indicating the degree of orderedness of dolomite could not be measured partly because of the coincidence and partly for the smaller quantity of dolomite.

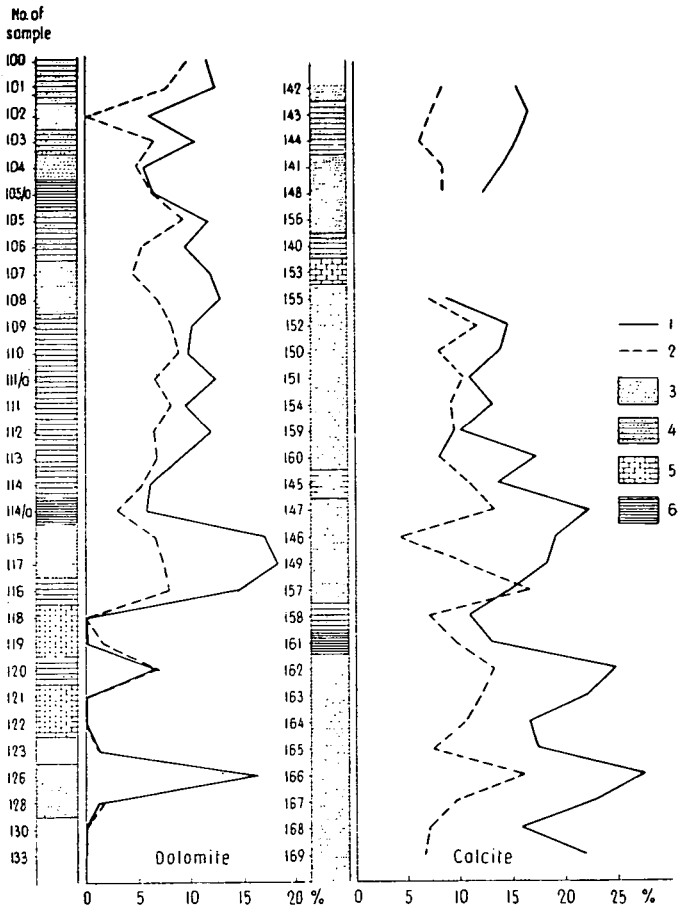

Fig. 4. Calcite and dolomite content of fraction less than 10 microns (legend see *Fig. 1.*)

SUMMARY

Calcite and dolomite quantities of the sandstones, aleurites, marls, lime-muds and clays deriving from the deep-bores of the Great Plain, were investigated. The data determined in the *X*-ray diffractograms were compared with those calculated from the gasometrically determined CO_2 content and values of peak intensities. Deviation was greater only in case of certain clayey samples, the other values remained within the limits of error. In respect of dolomite the results were identical, in general. Thus, in case of using the corresponding constants not only the quantities of clay

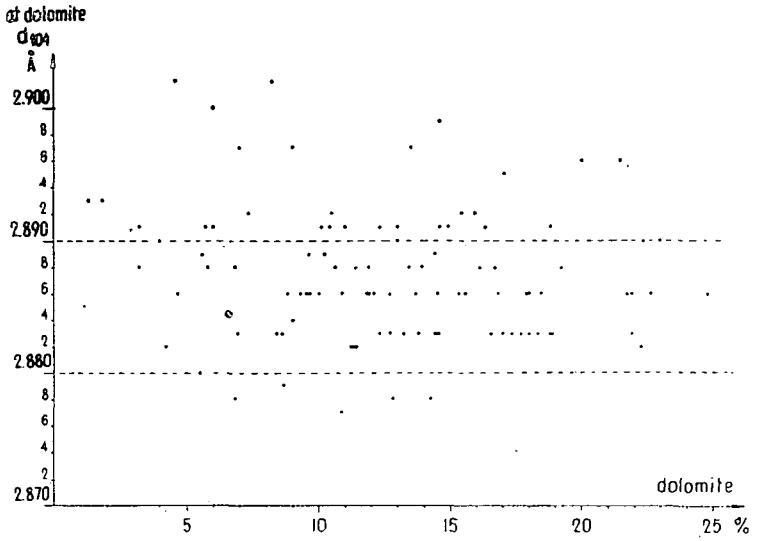

Fig. 5. Change of the composition of the dolomite in the samples on the basis of the d_{104} value

minerals, chlorite, quartz and feldspars but those of carbonates can also be computed from the *X*-ray diffractograms. This method is relatively rapid and investigations can be carried out in series. In case of preparation, however, specific care should be taken in homogenization.

In the samples investigated the dolomite was absent when the calcite content exceeded 50 per cent. Since the calcite-containing layer is nearly in contact with that of calcite and dolomite content, this can be attributed only to salinity changes.

Part of dolomite is a result of late diagenesis, which is proved partly by the coarser grain size (these separated out of the fraction of 10 microns), partly by the absence of gypsum and anhydrite.

Dolomite is for the most part of stoichiometric composition. On the basis of the d_{104} value of dolomite the calcium surplus can be observed only in a few samples and the displacement towards the magnesite composition was followed only in several samples.

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RAPID DETERMINATION OF CALCITE AND DOLOMITE FOR ROUTINE ANALYSIS BY GASOMETRY

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INTRODUCTION

Analysis of calcite and dolomite is a routine work in laboratories dealing with examination of mineral composition of rocks, and problems of dolomitization.

Several methods are well known, which are very different in their rapidity and accuracy according to demands.

The determination of Ca and Mg by complexometry connecting it with the determination of CO_2 offer a possibility to calculate the amounts of calcite and dolomite [MÜLLER, 1967]. Naturally in this case all the Mg is taken as belonging to the dolomite.

According to SMYKATZ—KLOSS cited by MÜLLER the DTA method may be considered more exact for determination of calcite and dolomite than the *X*-ray diffractometry, however, it gives correct results only in the case of relatively pure carbonate rocks.

A wide-spread method is the *X*-ray diffractometry. According to TENNANT and BERGER [1957] the ratio of amount of calcite and dolomite is proportional to the ratio of the peak heights $\frac{d_{cal}\,3{,}03\ \text{Å}}{d_{dol}\,2{,}896\,\text{Å}}$ and the relative amounts may be read from a calibration curve. The accuracy of this method is $\pm$ 5% in case of from 10 to 90 per cent dolomite content.

Knowing the relative calcite and dolomite content of the samples and determining the CO_2 content by gasometry the absolute amounts of the carbonates may be calculated [VAN MOORT, 1973; MOLNÁR, 1974].

A comparison of the accuracy of determination of calcite and dolomite in sedimentary rocks, by different methods is given by MEZŐSI [1975].

The aim of this work is to find a simple, rapid calcite and dolomite determination, which can be carried out in laboratories without *X*-ray diffractometer or derivatograph.

EXPERIMENTAL PART

This method is based on the fact that calcite dissolves rapidly and perfectly in 1:1 HCl at room temperature, but dolomite dissolves after some time and very slowly.

Measurement of CO_2 released treating the sample by 1:1 hydrochloric acid is carried out by gasometry. 1:1 HCl releases CO_2 from carbonates. The volume of CO_2 and the volume of air in the tube is determined at room temperature and atmospheric pressure. The gas mixture is passed into KOH solution several times in order to discharge CO_2. The volume of the rest of gas is measured

again at room temperature and atmospheric pressure. The difference between the two volume corresponding to the volume of the CO_2 is reduced to standard temperature and pressure on the basis of fundamental gas equation. The weight of CO_2 is calculated in the following way:

$$1 \text{ ml } CO_2 = 0{,}1976 \text{ g } CO_2 \qquad (1)$$

$$CO_2\% = \frac{0{,}1976\ V}{A} \qquad (2)$$

where V means the reduced volume of CO_2,
A means the weight of sample.

According to experiments the results are reliable, the maximum deviation from the average value is ± 1 per cent.

Dolomite, magnesite and calcite from Ratkószuha were used in the experiments. Samples were ground in agate mortar to grain size $d \leqq 60\ \mu$.

According to our experiments 0,1 g calcite dissolves perfectly in 10 ml 1:1 hydrochloric acid within 15 seconds at room temperature, but the dissolution of dolomite does not start within 60 seconds. Therefore, the CO_2 content measured after 30 seconds reaction time at room temperature gives the amount of CO_2 belonging to the calcite content of the sample.

Weighing in another 0,1 g portion of the sample and determining the CO_2 content after 4—5 minutes boiling, the CO_2 content both of the calcite and dolomite was determined. The difference of the two measurements gives the CO_2 of the dolomite present in the sample.

However, a part of the CO_2 released at room temperature is dissolved in the 1:1 hydrochloric acid and this part of the gas can be expelled only after boiling. It was assumed, that the volume of CO_2 dissolved at room temperature and at constant volume of HCl is proportional to the volume of the total CO_2.

Mixtures were made from pure calcite and clay mineral free of carbonate, the calcite content of the series changed between 10—100 per cent. The volume of CO_2 of separate portions was measured at room temperature and after boiling. Results can be seen in Table 1. CO_2 determined at room temperature and after boiling differ from each other, but they are proportional *(Fig. 1)*.

On the curve *Fig. 1* three sections may be distinguished corresponding to samples of 0—30 per cent, 30—80 per cent and 80—100 per cent calcite content, respectively.

TABLE 1

Calcite content of mixtures made from pure calcite and clay mineral free of carbonate

Calcite % in mixture	CO_2 %	Calcite %	CO_2 %	Calcite %
	measured at room temperature		measured after boiling	
9,77	1,94	4,39	4,45	10,09
19,91	5,22	11,84	8,80	19,97
30,59	9,73	22,08	13,66	31,00
40,23	12,43	28,22	17,28	39,23
50,54	15,74	35,73	21,88	49,67
60,22	18,72	42,50	26,76	60,75
70,54	21,92	49,77	31,18	70,77
80,44	26,67	60,55	35,59	80,79
90,12	32,39	73,53	40,27	91,41
100,00	34,51	78,34	44,26	100,40

This is in connection with the solution of the CO_2 in the hydrochloric acid. By the calibration curve given the quantity of CO_2 belonging to the calcite content of the samples can be determined on the basis of CO_2 content measured at room temperature.

The method was controlled by measuring the CO_2 content of mixtures of calcite and dolomite. Results are shown in Table 2. Quantity of calcite and dolomite measured and calculated from calibration curve corresponds to the theoratical values well enough.

Some measurements were carried out in order to study the effect of grain size on the accuracy of this method. Determining the calcite and dolomite content of the calcite-dolomite standards of 10—30 μ and 30—50 μ fractions, it was found, that results were independent of grain size within this range (Table 3.)

If other minerals containing carbonate are present besides calcite and dolomite, it can effect on the results of measurements. If these carbonates dissolve in 1:1 hydrochloric acid at room temperature, the calcite content determined by this method will be higher, and dolomite will be lower than the theoretical value. In the presence

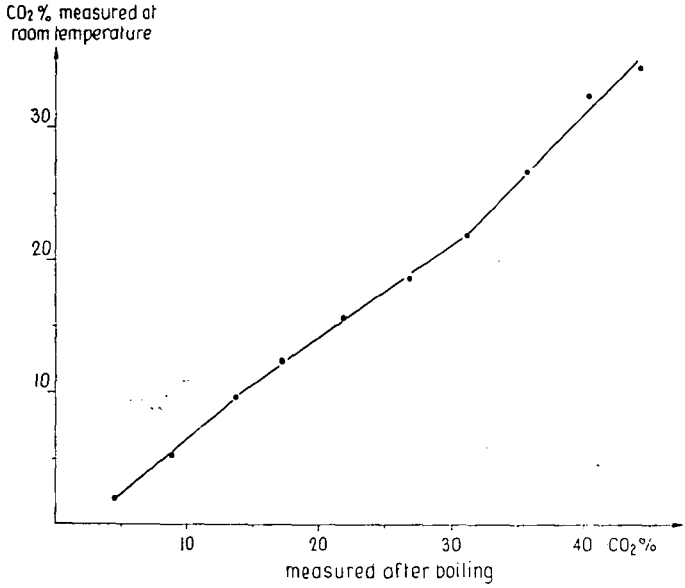

Fig. 1. Calibration curve for determination of calcite content.

TABLE 2

Comparison of the amount of the calcite and dolomite measured and calculated

Calcite/dolomite ratio	CO_2 measured		CO_2% (calcite)	CO_2% (dolomite)	Calcite %		Dolomite %	
	at room temperature	after boiling			measured	calculated	measured	calculated
20/80	5,0	45,6	8,6	37,0	19,5	20,3	77,7	77,1
50/50	15,7	44,8	22,3	22,5	50,6	50,1	47,2	46,8
80/20	26,7	45,0	36,0	9,0	81,7	80,0	18,9	18,4

TABLE 3

Calcite and dolomite content of samples of different grain size

Grain size	Calcite %		Dolomite %	
	calcu-lated	measur-ed	calcu-lated	measur-ed
10—30 μ	50,2	51,0	49,8	49,0
30—50 μ	50,6	51,1	49,4	48,9

of carbonate compounds soluble only by boiling, the determination of the calcite is exact, but values concerning the dolomite content will be higher including the CO_2 content both of dolomite and other carbonates.

The behaviour of the magnesite was studied under the conditions applied. It did not dissolve at all at room temperature, and only 20 per cent was dissolved even if it was boiled for 5 minutes.

The amount of calcite of samples containing also magnesite can be determined exactly, but the presence of magnesite results failure in the determination of dolomite content.

In the case of standard samples calcite and dolomite content calculated and measured correspond well, therefore, core samples from the southern part of the Great Hungarian Plain were studied in this way. Results are shown in Table 4.

Determinations of calcite and dolomite content of the same samples were already carried out by X-ray diffractometry combined with gasometric total CO_2 determination as mentioned previously. Comparison of calcite and dolomite content determined by these two different methods in the same samples is compiled in Table 5.

TABLE 4

Calcite and dolomite content of core samples from the southern part of the Great Hungarian Plain

Samples	CO_2 % measured		CO_2 %		Calcite %	Dolomite %
	at room temperature	after boiling	(calcite)	(dolomite)		
Upper Pannonian aleurite 1660 m	2,4	11,7	5,0	6,7	11,3	14,0
Lower Pannonian sandstone 2061 m	1,0	10,9	3,2	7,7	7,3	16,1
Lower Pannonian clay marl 4140 m	2,6	9,1	5,2	3,9	11,8	8,2
Lower Pannonian clay marl 4152 m	1,9	16,7	4,4	4,2	10,0	8,8
Lower Pannonian marlstone 4153 m	9,5	10,5	13,5	3,2	30,6	6,7
Miocene aleurite 4248 m	2,8	8,6	5,6	4,9	12,7	10,3

TABLE 5

Comparison of calcite and dolomite content of samples measured by different methods

Samples	Calcite % measured		Dolomite % measured	
	by gasometry	by *X*-ray diffr.	by gasometry	by *X*-ray diffr.
Upper Pannonian aleurite 1660 m	11,3	9,5	14,0	15,8
Lower Pannonian sandstone 2061 m	7,3	6,1	16,1	17,1
Lower Pannonian clay marl 4140 m	11,8	12,3	8,2	7,8
Lower Pannonian clay marl 4152 m	10,0	9,9	8,8	8,9
Lower Pannonian marlstone 4153 m	30,6	33,9	6,7	3,7
Miocene aleurite 4248 m	12,7	12,8	10,3	10,2

SUMMARY

Determination of calcite and dolomite by gasometry is a rapid, suitable method for routin examinations, it is based on the fact, that 1:1 hydrochloric acid dissolves calcite at room temperature under certain duration, whereas dolomite remains unattacked within the conditions given, and either calcite or dolomite dissolves after 5 minutes boiling.

Measuring the volume of CO_2 of the first portions of the sample at room temperature the quantity of calcite, whereas measuring the CO_2 volume of the second portion after boiling, the quantity of calcite+dolomite can be determined.

Since the CO_2 partly dissolves in the solution at room temperature the CO_2 content have to be corrected by the calibration curve determined experimentally.

Advantage of this method is that it can be carried out with simple equipments, it does not need any special pretreatment, only a grinding to $d \leqq 60\,\mu$ grain size.

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DIFFERENTIATION POSSIBILITIES OF PRIMARY AND SECONDARY ORGANIC MATTERS IN THE NEOGENE SEDIMENTS OF THE SOUTH GREAT PLAIN (HUNGARY)

J. BOROS

ABSTRACT

The present paper suggests a method to differentiate the organic matter of primary and secondary character on the basis of the investigations of core samples of two deep-bores drilled in the Neogene sediments of the South Great Plain (Hungary). The two deep-bores are located in the "Hódmezővásárhely—Makó" trench. On the basis of the investigation of the soluble organic matter content of the rock types of clay-marl, lime-marl and aleurite it could be stated that the strata sequences of the bores Makó-1 and Hód-1 can be divided into three great units out of which the lower one contains the Tortonian and the predominantly pelitic sequence of the Lower Pannonian being in accordance with the deep-structure; these can be regarded one unit. The middle part is of Lower Pannonian, the upper one of Upper Pannonian age. On the basis of the bitumen content the bore of Hód-1 represents a neritic-pelagic environment while the bore Makó-1, is of near-shore location. As to the suggested method is was also stated that the soluble organic matter of the Lower Pannonian is rather of secondary character, and the hydrocarbon genesis of the same features took place in the Upper and Lower Pannonian while this proved to be dissimilar in the Miocene.

CHANGE OF THE SOLUBLE ORGANIC MATTER CONTENT AS A FUNCTION OF DEPTH

Investigation methods

The soluble, non-volatile organic matter content of the core samples of bores drilled in the "Hódmezővásárhely—Makó" trench was investigated. The part of the disperse organic matter which can be extracted by organic solvents, i.e. the so-called bitumen content was extracted by means of the SOXHLET apparatus. Subsequent extractions were applied: the rock sample was first extracted by chloroform to obtain the bitumen-A, and after dissolution by hydrochloric acid the extraction with benzene-ethanol was carried out. The extract obtained in this way is called bitumen-C (in the following: Bit-A and Bit-C). The extracts Bit-A and Bit-C were divided into three fractions by means of column chromatography. To characterize the relation between the bitumen values and depth calculation of regression was carried out concerning the whole investigated strata sequence as well as separatedly in case of the Upper, Lower Pannonian and Miocene samples. This computation has been necessary since the tendency of change can be incompletely followed because of the fluctuation of the values.

Change of Bit-A and Bit-C as a function of depth in the bore Makó-1

The Bit-A values of the core samples of the bore Makó-1 varies between $20 \cdot 10^{-3}$ and $61 \cdot 10^{-3}$ per cent. In three samples it shows very high values: in 2500 metres $56 \cdot 10^{-3}$ per cent, in 1400 metres $48 \cdot 10^{-3}$ per cent and in 3180 metres $61 \cdot 10^{-3}$

per cent (*Fig. 1* and Table 1). On the basis of regression computed to the investigated sequence of strata the value of Bit-A increases with increasing depth. This corresponds to the statement of JEREMENKO [see: MEINHOLD, 1965] as to which the quantity of neutral bitumen increases with the age. When having computed these values to the individual Upper and Lower Pannonian samples the regression lines have shown decreasing tendency as a function of depth. Because of the small value of the regression coefficient this decrease is very slight, in case of the Lower Pannonian samples the Bit-A is practically independent of depth. On the basis of regression at the boundary of the Lower and Upper Pannonian the quantity of Bit-A shows a sudden increase. This may be connected with the more progressive measure of the continuous transformation of the organic matter and with the strengthening of the secondary character of Bit-A. All these correlate with the change in sedimentary environment fixed by the geologists at the boundary of the Upper and Lower Pannonian.

The value of Bit-C shows considerably greater fluctuation than that of Bit-A, its quantity varies from $20 \cdot 10^{-3}$ to $140 \cdot 10^{-3}$ per cent. Its value is extremely high in 1000 metres ($69 \cdot 10^{-3}$%), in 1400 metres ($69 \cdot 10^{-3}$%), in 2100 metres ($140 \cdot 10^{-3}$%), in 2200 metres ($106 \cdot 10^{-3}$%) and in 3180 metres ($74 \cdot 10^{-3}$%). On the basis of the regression line the value of Bit-C decreases with increasing depth, probably as a result of the Bit-C→Bit-A transformation (*Fig. 2* and Table 1).

According to the investigations of TISSOT [1971] the quantity of the heterocompounds of great molecular weight decreases with increasing depth because of the formation of the compounds poor in heteroelements or being totally in lack of these. He assumed that the following transformation takes place:

Kerogen → compounds containing O, N, S heteroelements (acidic bitumen) → hydrocarbons, resins, asphalts (neutral bitumen).

Similar transformation is referred by the experiments of LOUIS and TISSOT [1967] carried out on samples originating from the Paris-Basin. They treated the

TABLE 1

Bitumen contents of the core samples of the bore Makó-1

No.	Depth	Bit-A·10^{-3}	Bit-C·10^{-3}	Rock type
1	805,30— 808,00	21	38	clay-marl
2	1000,00—1006,00	39	68	clay-marl
3	1100,50—1102,70	36	31	clay-marl
4	1403,50—1404,05	29	63	aleurite
5	1404,50—1405,10	48	69	clay-marl
6	1500,10—1501,50	23	20	aleurite
7	2102,20—2102,40	25	140	aleurite
8	2150,00—2150,80	32	25	aleurite
9	2196,00—2196,50	31	106	aleurite
10	2351,00—2352,05	34	49	aleurite
11	2500,14—2500,21	46	51	aleurite
12	2722,00—2722,35	24	51	clay-marl
13	3064,45—3064,51	38	23	clay-marl
14	3180,15—3180,20	61	64	clay-marl
15	3290,00—3290,20	38	48	clay-marl
16	3490,37—3490,42	32	24	clay-marl
17	3951,83—3952,00	33	29	clay-marl

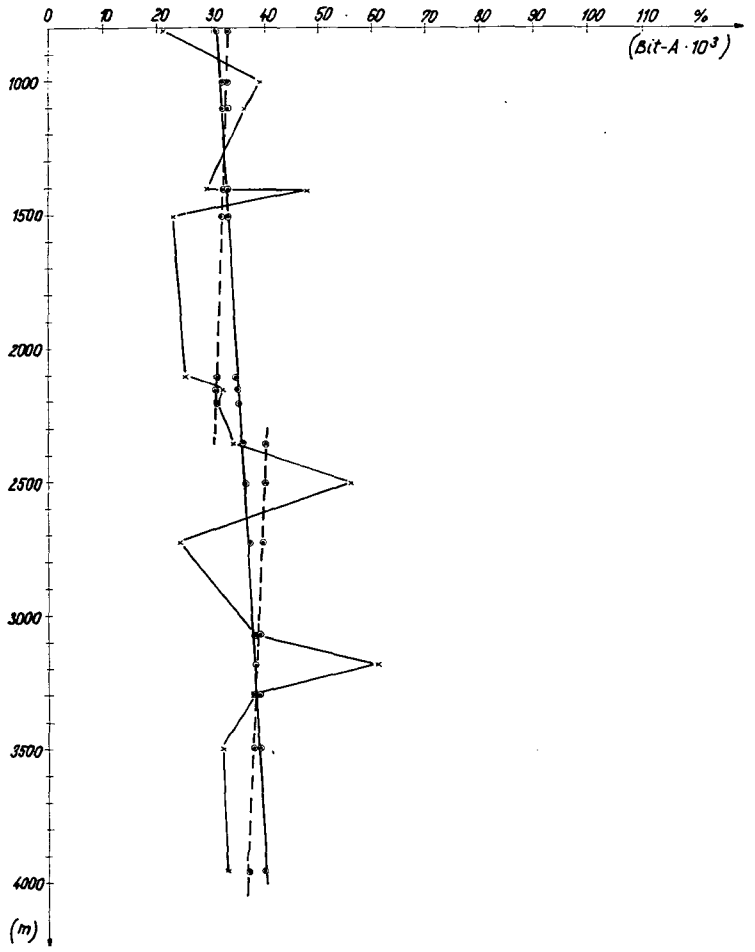

Fig. 1. The values of Bit-A from the Makó-1 drilling in the function of the depth

rock samples with such pressure and temperature values which are predominant in the deeper parts of the basin. They observed the increase of the quantity of neutral bitumen and assumed this process to take place through the formation of acidic bitumen.

In our investigations the Bit-C corresponds to the acidic, the Bit-A to the neutral bitumen; consequently, after TISSOT the kerogen → Bit-C → Bit-A transformation is supposed.

On the basis of the investigation of core samples this transformation cannot be followed in such an unambiguous manner. The quantities of Bit-A and Bit-C of the single samples are influenced by the environmental factors, the quantity of the organic matter of the sediment, the quality and accidental migration of the organic components.

Regarding the computation carried out separatedly on the Upper and Lower Pannonian samples the value of Bit-C increases in the Upper Pannonian and decreases

in the Lower Pannonian samples. This may probably be connected to the consecutive feature of transformation, in the Upper Pannonian the transformation of kerogen → Bit-C, in the Lower Pannonian that of Bit-C → Bit-A could follow.

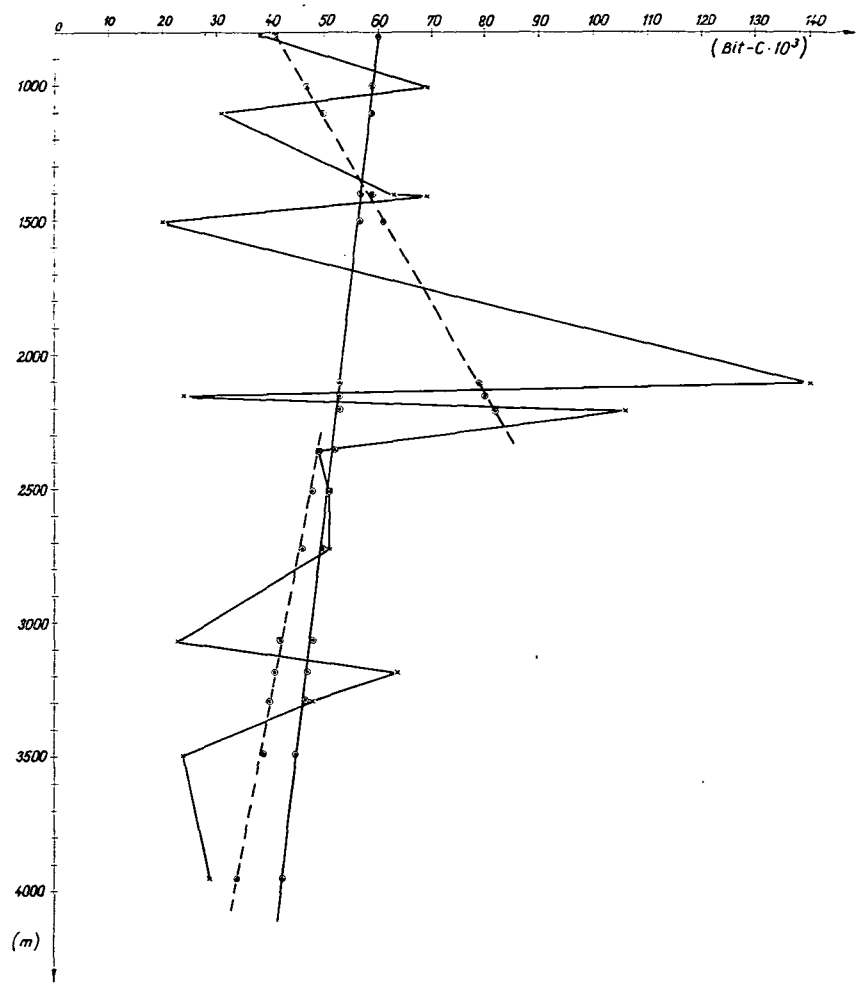

Fig. 2. The values of Bit-C from the Makó-1 drilling in the function of the depth

Change of Bit-A and Bit-C as a function of depth in the bore Hód-1

The bore Makó-1 did not reach the Miocene strata while the bore Hód-1 located NW of it in a distance of about 5 km was stopped in Miocene formations. Out of the core samples of the bore of Hód-1 two samples of the Upper Pannonian were investigated which alone could not be evaluated thus it was carried out only together with the Lower Pannonian ones.

The quantity of Bit-A varies between $14 \cdot 10^{-3}$ and $249 \cdot 10^{-3}$ per cent. Extremely high values were obtained in 4264 m ($95 \cdot 10^{-3}$), in 4538 m ($115 \cdot 10^{-3}$) and in

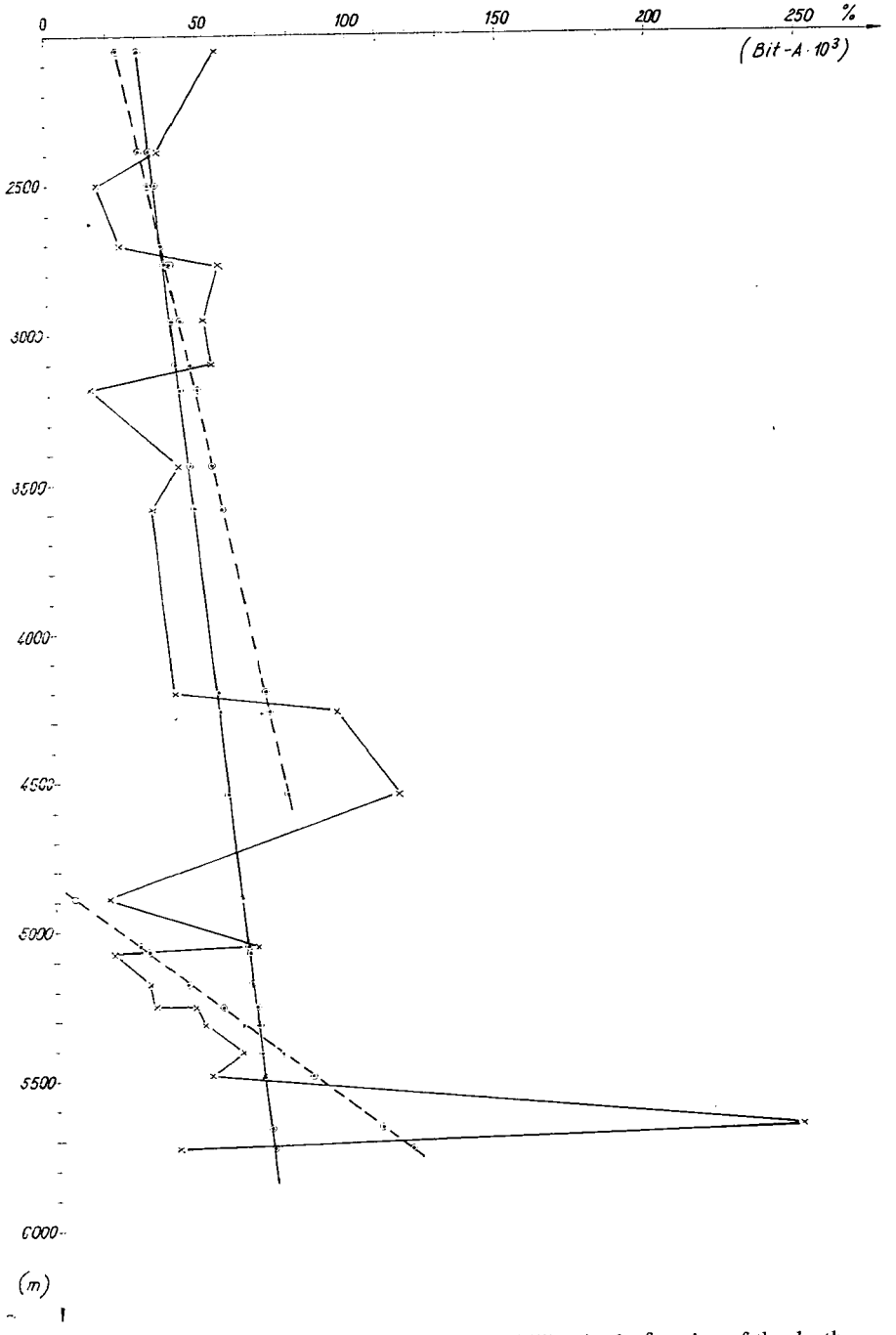

Fig. 3. The values of Bit-A from the Hód-I drilling in the function of the depth

TABLE 2

Bitumen contents of the core samples of the bore Hód-1

No.	Depth	Bit-A·10^{-3}	Bit-C·10^{-3}	Rock type
1.	2050,57—2050,66	56	69	clay-marl
2.	2386,44—2386,65	37	53	clay-marl
3.	2501,62—2501,68	17	67	fine aleurite
4.	2700,85—2701,04	24	59	fine aleurite
5.	2759,17—2759,40	56	48	clay-marl
6.	2954,17—2954,27	52	69	fine aleurite
7.	3098,00—3099,00	54	64	clay-marl
8.	3182,20—3182,60	14	53	clay-marl
9.	3437,30—3438,30	43	46	clay-marl
10.	3584,50—3584,80	34	58	clay-marl
11.	4200,00—4200,40	40	49	fine aleurite
12.	4264,65—4264,75	95	55	fine aleurite
13.	4538,32—4538,78	115	56	marl
14.	4888,45—4888,60	18	98	aleurite
15.	5054,51—5054,60	67	125	clay-marl
16.	5072,72—5072,94	19	122	lime-marl
17.	5174,15—5174,32	31	109	lime-marl
18.	5252,52—5252,68	46	97	lime-marl
19.	5255,71—5255,89	33	71	marl
20.	5311,39—5311,43	49	77	lime-marl
21.	5407,30—5407,45	62	79	lime-marl
22.	5483,43—5483,60	51	106	lime-marl
23.	5660,64—5660,80	249	225	lime-marl
24.	5732,11—5732,28	40	109	marl

5660 m ($249 \cdot 10^{-3}$). On the basis of regression computed to the whole investigated sequence the value of Bit-A is increasing similarly to the bore Makó-1 (*Fig. 3,* Table 2). Taking the separate computation to the Lower Pannonian and Miocene samples it can be stated that the quantity of Bit-A increases both in the Lower Pannonian and in the Miocene. This increase is of much higher degree within the Miocene than in the Lower Pannonian ($\operatorname{tg} \alpha = 2.16 \cdot 10^{-5}$ and $13.31 \cdot 10^{-5}$). In the Lower Pannonian the secondary character resp. transformation-degree of the bitumen is probably increasing. This is the same in the Miocene, too, with the difference that primary bitumen is replaced by secondary one.

The boundary between the Lower Pannonian and Miocene was drawn between 4550 and 4850 metres since on the basis of the bitumen content the change follows in this depth interval which is extraordinarily conspicuous in case of the Bit-C values. This delineation is supported by the statement of K. SZENTGYÖRGYI [1973], according to which in the Lower Pannonian sequence much sandstone can be taken into consideration down to 4450 metres.

The structure of the strata sequence changes from 4450 metres, this section is characterized by the frequent alternation of thin sandstone, aleurite and clay-marl. The proportion of sandstones decreases. The Tortonian sediments show similar petrographic formations. These factors are, however, significant from the point of view of the organic matter.

The value of Bit-C varies between $46 \cdot 10^{-3}$ and $225 \cdot 10^{-3}$ per cent. It produces extreme values in 5054 and 5660 metres of $125 \cdot 10^{-3}$ resp. $225 \cdot 10^{-3}$ per cent (*Fig. 4.* and Table 2). On the basis of regressions the tendency of changes increases regarding the whole sequence, in the Lower Pannonian decreases, and in the Miocene increases.

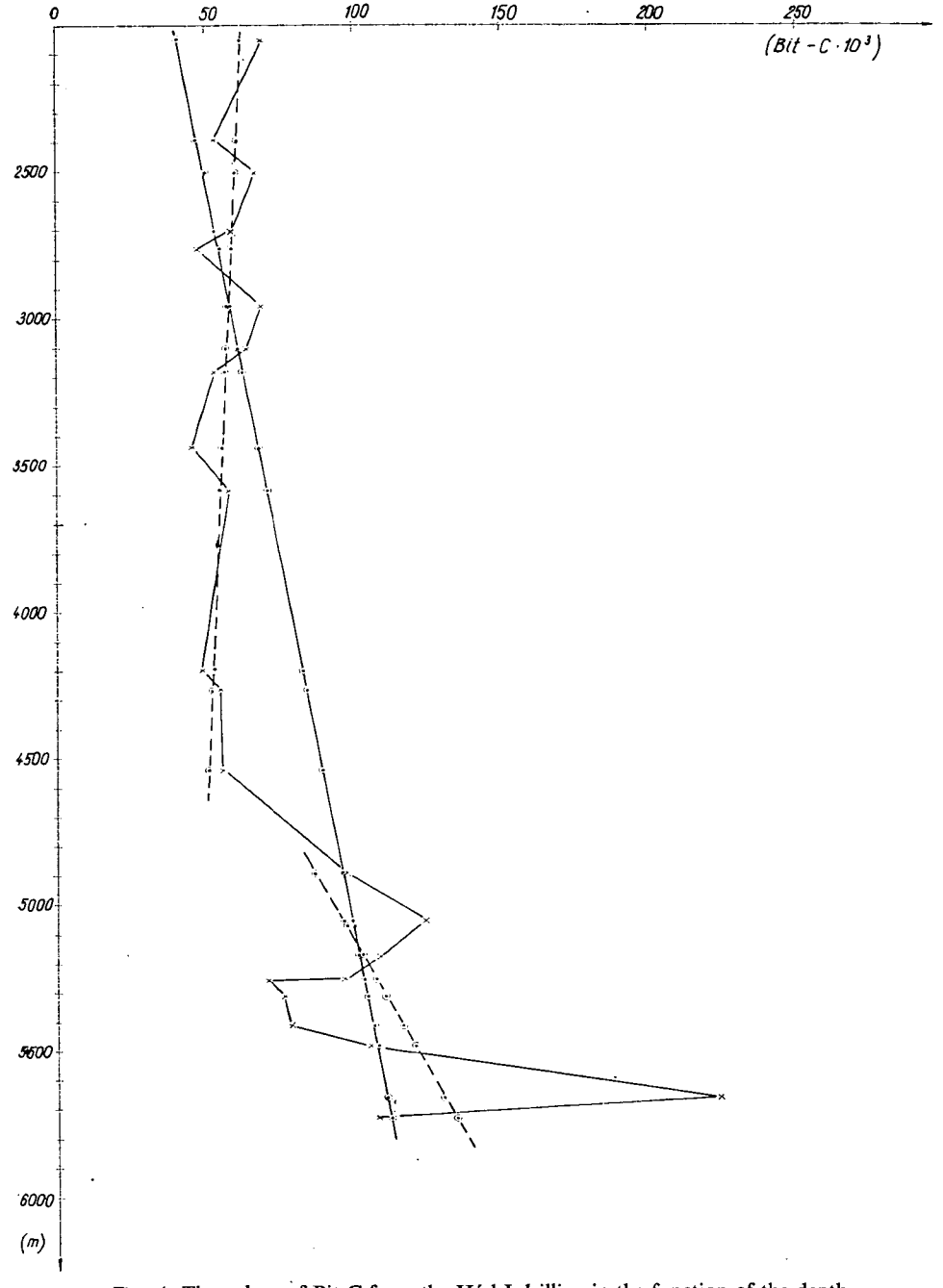

Fig. 4. The values of Bit-C from the Hód-I drilling in the function of the depth

As to our assumption this decrease can be attributed to the strengthening of the Bit-C→Bit-A process as a result of the consecutive character of the Bit-A formation process, as it has been characteristic also of the Lower Pannonian samples of the bore Makó-1. On the contrary, the increase following in the Miocene may relate to progression of the formation process of Bit-A. The quantity of bitumens extracted from the samples of the bore Hód-1 is greater than in case of the bore Makó-1. This difference in quantities can be traced back to the location of the bores in the sedimentary basin. On the basis of the bore Hód-1 in the "Hódmezővásárhely—Makó" trench a pelagic facies of several metres depth of water, of H_2S-content and of negative redox potential existed [M. MUCSI, 1973]. The bore Makó-1 is of near-shore position while the Hód-1 bore lies farther from the shore, as it can be proved on the basis of bitumen content.

POSSIBILITY OF DISTINCTION OF PRIMARY AND SECONDARY CHARACTER OF THE SOLUBLE ORGANIC MATTER

The change of the quantity of Bit-A and Bit-C has till now explained by the thermal degradation of the organic matter. It is not enough to take into consideration the chemical transformations took place in the organic matter; as regarding the explanation of the changes since as it was mentioned above other factors may also play decisive role in the quantitative formation of the organic matter. One of these factors is the migration itself thus in the course of the investigation we tried to obtain some information on the primary resp. secondary character of the organic matter.

As to our assumption to decide the primary resp. secondary character of the organic matter, the quotient Bit-C/Bit-A can be applied completing with the values Bit-A and Bit-C. Since Bit-A is a much more mobile component, in the places where the organic matter can be considered to be of secondary character the Bit-A value should reach a maximal value.

Owing to its more polar character, the Bit-C is capable to adsorption and is bound rather to its formation place, thus, it can be assumed that its greater quantity relates to the primary character of the organic matter. When this assumption can be accepted within certain limits, the value of the quotient Bit-C/Bit-A will be low in case of primary, and high in case of secondary organic matter and this can be connected with the mobility of Bit-A and *in situ* character of Bit-C. The quotient alone is insufficient to decide this problem since in the case when both the Bit-A and the Bit-C values are high, i.e. the value of the quotient does not differ from the average, the presence of organic matter of secondary character is improbable in the samples (though the quotient value relates to this fact). Consequently, taking into consideration the values of Bit-A and Bit-C it can be said that the high Bit-C/Bit-A value relates to the primary, the low Bit-C/Bit-A value to the secondary character of the organic matter. Ideally primary and secondary character was found in any core samples, either, thus the terms "primary" and "secondary" refer to predominantly primary and predominantly secondary characters. Between these two extreme stages a medium one can be distinguished which, on the basis of the relative quantitites of Bit-A and Bit-C could be classified as "rather primary" and "rather secondary" categories.

Taking into account all these factors it can be stated that in case of the bore of Makó-1 the organic matter can be considered to be of primary character in the samples of aleurite and clay-marl type deriving from 1403 m (4), 2102 m (7), 2196 m (9) and 2722 m (12); while the samples of aleurite and clay-marl type deriving from 1100 m

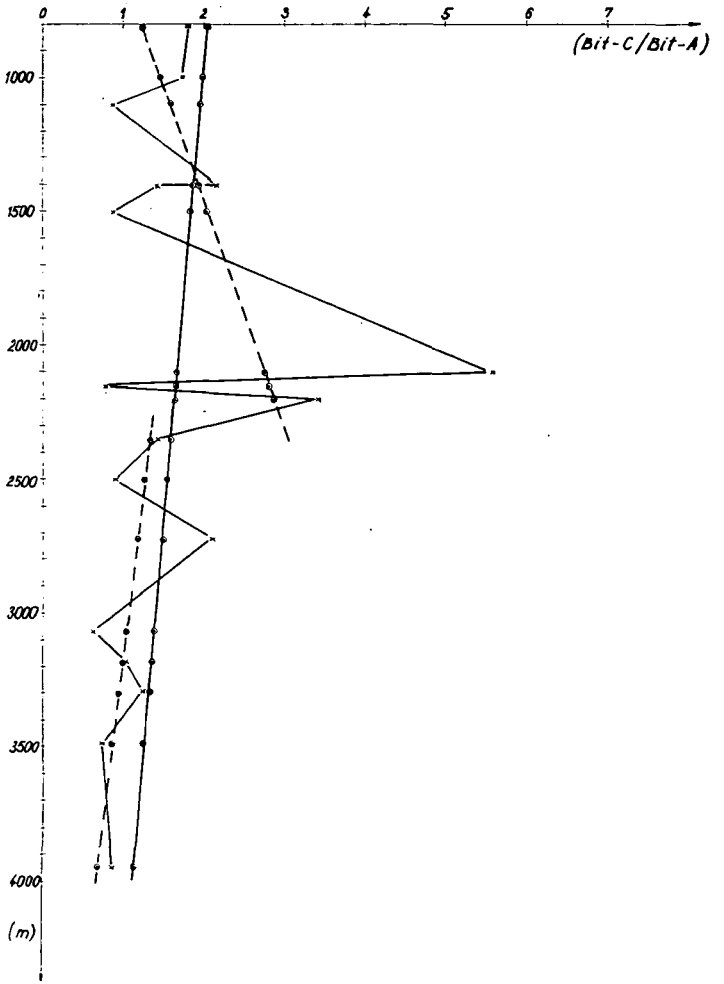

Fig. 5. The values of Bit-C/Bit-A from the Makó-1 drilling in the function of the depth

(3), 2351 m (10), 2500 m (11), 3064 m (13) and 3290 m (15) can be regarded secondary types. In the other samples both the primary and the secondary character can be determined. Within these samples, however, the "rather primary" and "rather secondary" character can be distinguished. *E.g.* in the aleurite and clay-marl samples though containing both types the primary character is predominant in 805 m (1), 1000 m (2), 1404 m (5) and 3180 m (14). In case of the bore Makó-1 the change of the quotient Bit-C/Bit-A with the depth resp. the run of the regression lines are shown in *Fig. 5.*, their values are listed in Table 3.

Based on the regression line, the value of the quotient decreases with increasing depth and this relates to the weakening of the primary and gradual predominancy of the secondary character. In the Upper Pannonian the value of Bit-C/Bit-A is greater than in the Lower Pannonian and increases parallel with the depth, thus in

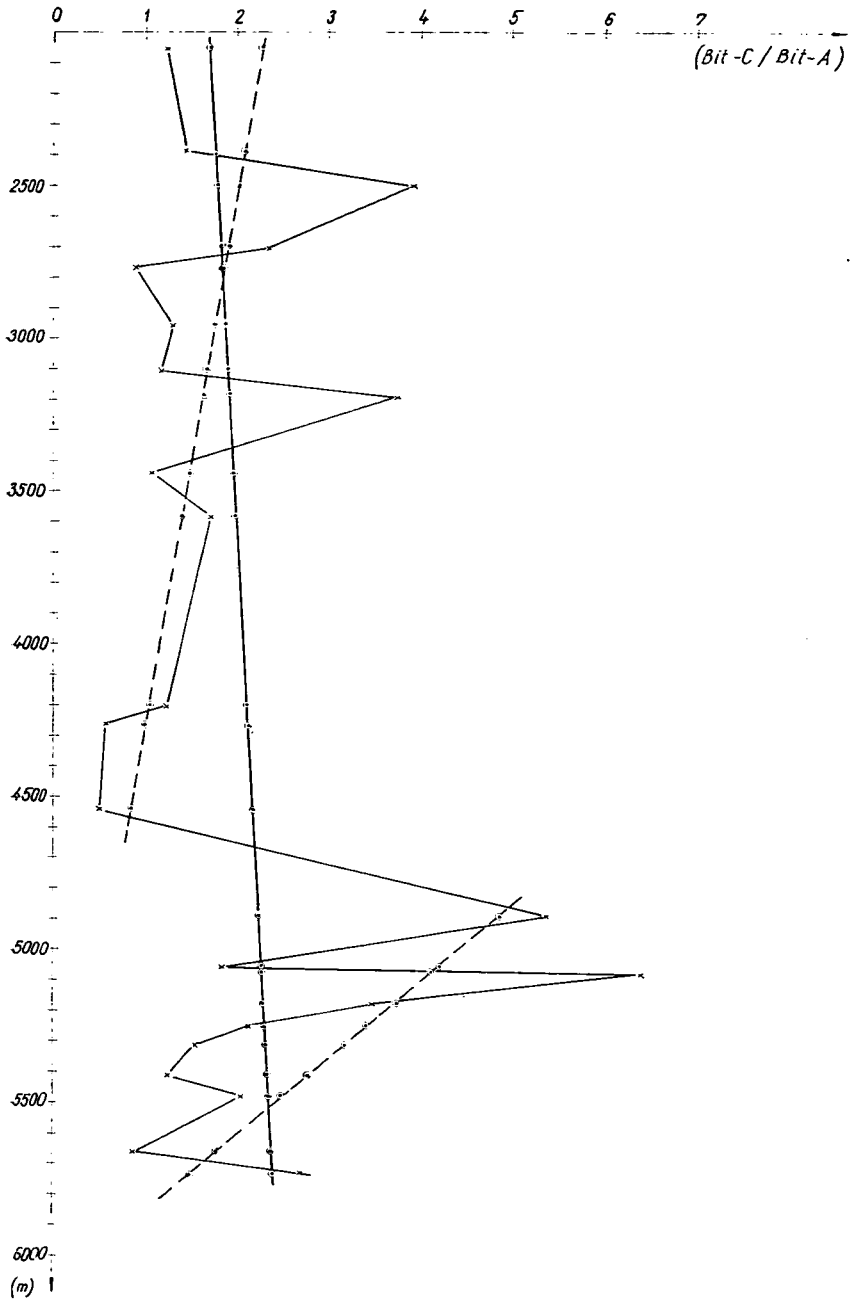

Fig. 6. The values of Bit-C/Bit-A from the Hód-I drilling in the function of the depth

TABLE 3

Bit-C/Bit-A values of the bores Makó-1 and Hód-1

Bore	No.	Bit-C/Bit-A	Bore	No.	Bit-C/Bit-A
M-1	1	1,81	Hód-1	1	1,23
M-1	2	1,74	Hód-1	2	1,43
M-1	3	0,86	Hód-1	3	3,94
M-1	4	2,17	Hód-1	4	2,36
M-1	5	1,44	Hód-1	5	0,85
M-1	6	0,87	Hód-1	6	1,30
M-1	7	5,60	Hód-1	7	1,18
M-1	8	0,78	Hód-1	8	3,78
M-1	9	3,42	Hód-1	9	1,07
M-1	10	1,44	Hód-1	10	1,71
M-1	11	0,91	Hód-1	11	1,23
M-1	12	2,12	Hód-1	12	0,58
M-1	13	0,61	Hód-1	13	0,50
M-1	14	1,05	Hód-1	14	5,44
M-1	15	1,26	Hód-1	15	1,86
M-1	16	0,75	Hód-1	16	6,10
M-1	17	0,87	Hód-1	17	3,51
			Hód-1	18	2,11
			Hód-1	19	2,15
			Hód-1	20	1,57
			Hód-1	21	1,27
			Hód-1	22	2,08
			Hód-1	23	0,90
			Hód-1	24	2,73

the Upper Pannonian the value of the quotient is lower, decreases parallel with the depth, consequently the organic matter is rather of secondary character.

On the basis of the same aspects in the rock samples of fine aleurite, clay-marl and marl type the organic matter could be assigned to the secondary types in 2050 m (1), 2759 m (5), 2954 m (6), 3098 m (7), 4264 m (12) and 4538 m (13), while in the samples of clay-marl, marl and lime-marl type the organic matter is of primary character in 4888 m (14), 5072 m (16), 5174 (17), 5252 m (18) and 5732 m (24). In the transitional category, in the samples of clay-marl, lime-marl type the organic matter is rather of secondary character in 2386 m (2), 3437 m (9), 3584 m (10), 4200 m (11), 5311 m (20) and 5660 m (23), while in the samples of fine aleurite, clay-marl, marl, lime-marl type the organic matter is rather of primary character in 2501 m (3), 2700 m (4), 3182 m (8), 5054 m (15), 5255 m (19) and 5483 m (22). The values of the quotient are listed in Table 3, and are shown as a function of depth in *Fig. 6*. On the basis of the regression computed to the whole sequence the value of the quotient increases with increasing depth which may relate to the strengthening of the bitumen's primary character. In the Lower Pannonian the decrease means the strengthening of the secondary character down to the predominantly pelitic phase, the decrease from this level means the weakening of the primary character from the top downward. In general, it can be said that in the Lower Pannonian the organic matter of rather secondary type predominates in the core samples of both of the bore Hód-1 and Makó-1.

As it was mentioned above according to the kerogen→Bit-C→Bit-A transformation a genetic relation can be assumed between Bit-A and Bit-C. Owing to the other factors influencing the quantity of organic matter this relation cannot be

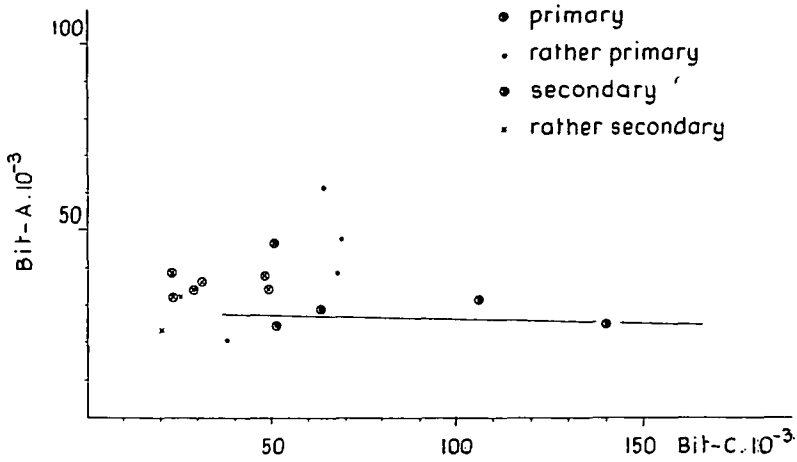

Fig. 7. The values of Bit-A from the Makó-1 drilling in the function of the Bit-C

unambiguously followed. On the basis of the factors used to decide the primary or secondary character of the organic matter a relation between Bit-A and Bit-C was found when taking into account the samples of primary character. In case of the bore Makó-1 plotting Bit-A as the function of Bit-C the points fall onto one straight line *(Fig. 7)*. Out of the samples belonging to the primary category of the transitional group the samples 14 and 5 are exceptions because of the stronger effect of the secondary character.

In case of the bore Hód-1 the samples containing primary organic matter lie along two straight lines *(Fig. 8)*. Taking into consideration the distribution according to ages it can be stated that the straight line of greater rise is accompanied by the

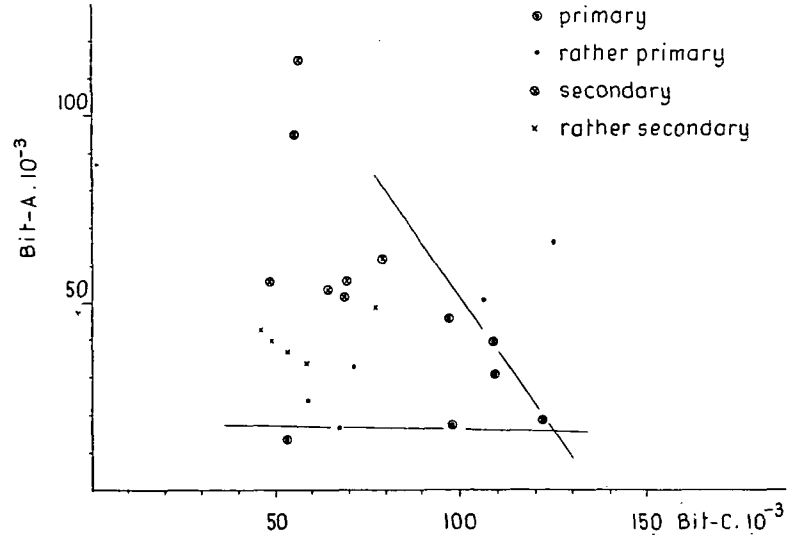

Fig. 8. The values of Bit-A from the Hód-I drilling in the function of the Bit-C

Miocene that of smaller rise by Lower Pannonian samples. From the bore Makó-1 Upper and Lower Pannonian samples were investigated. In case of the samples of Upper and Lower Pannonian age of both drills the rise of the straights are nearly of the same rise *(Figs. 7 and 8)*, from which the hydrocarbon genesis of similar character can be concluded. On the basis of the two straights obtained in the core samples of the bore Hód-1 it can be assumed that in the Miocene and in the Lower Pannonian hydrocarbon genesis of different character took place.

As a result of the migration of the organic matter not only the value of the Bit-C/Bit-A quotient is changing but a relative difference occurs also in the composition of the bitumens. This can be explained by the difference of mobility of the fractions obtained after the column chromatographic separation of bitumens (fraction I is the

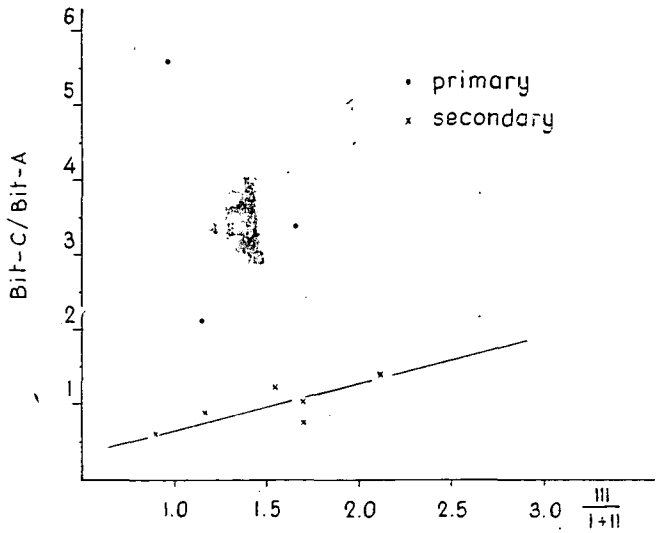

Fig. 9. The values of Bit-C/Bit-A from the Makó-1 drilling in the function of the III/I+II

most mobile, fraction III is least mobile, the hydrocarbons, neutral resins and acidic resins are contained by the I, II and III fractions). It is to be noted that the separation by column chromatography was carried out in the samples in which this proved to be possible as regarding the quantity of the organic matter.

The investigations of GY. GRASSELLY and M. HETÉNYI [1974] relate to the changes deriving from the different mobilities of the fractions, and these emphasized the primary character of the relation between C_{org} and the organic matter of greater molecular weight and containing also heteroelements and extracted by solvent mixture.

They stated that the quantity of chloroform bitumen extracted from sandstones (where the bitumen is certainly of secondary origin) is great, out of the fractions the first is predominating. As to their investigation results in addition to the quantity of chloroform bitumen the column chromatographic fraction can also be used to decide the primary and/or secondary characters of bitumens.

On the basis of all these factors and theoretical considerations the Bit-C/Bit-A quotient should be in connection with the quotient of fractions: III/I+II (see Table

TABLE 4

III/I+II values of the bores Makó-1 and Hód-1

Bore	No.	III/I+II	Bore	No.	III/I+II
M-1	8	1,70	Hód-1	3	1,55
M-1	9	1,65	Hód-1	4	1,11
M-1	10	2,11	Hód-1	5	1,67
M-1	11	1,17	Hód-1	6	1,60
M-1	12	1,14	Hód-1	7	1,45
M-1	13	0,90	Hód-1	8	0,56
M-1	14	1,70	Hód-1	9	1,22
M-1	15	1,55	Hód-1	10	1,33
M-1	16	1,15	Hód-1	11	0,97
M-1	17	2,17	Hód-1	12	0,63
			Hód-1	13	0,43
			Hód-1	14	0,86
			Hód-1	15	0,21
			Hód-1	19	0,80
			Hód-1	20	0,99
			Hód-1	21	1,63
			Hód-1	22	0,49
			Hód-1	23	0,22
			Hód-1	24	0,63

4). In case of both drills plotting the Bit-C/Bit-A as a function of fractions III/I+II, the samples of organic matter of secondary character lie along a straight line (*Figs. 9* and *10*) which may prove the relation between the two quotients in case of the changes followed during migration.

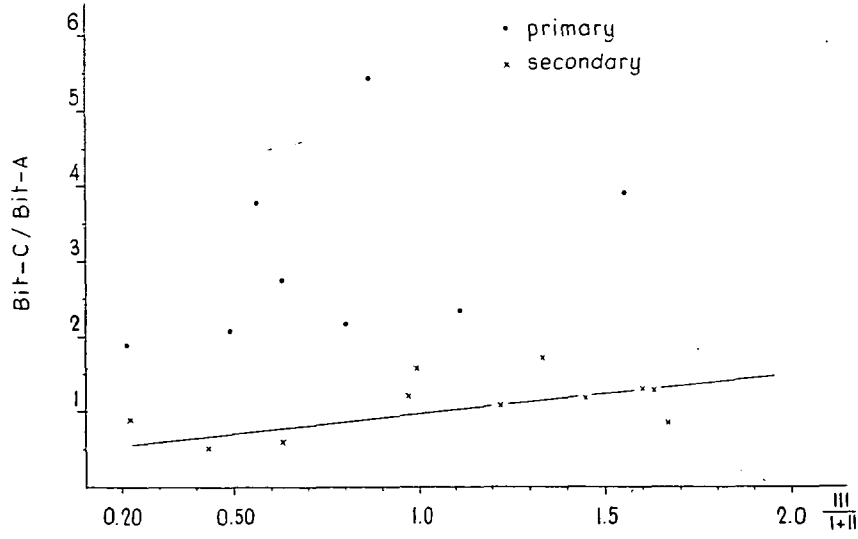

Fig. 10. The values of Bit-C/Bit-A from the Hód-I drilling in the function of the III/I+II

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BOOK REVIEWS

KAHLER, F.: FUSULINIDEN AUS T'IEN-SCHAN UND TIBET MIT GEDANKEN ZUR GESCHICHTE DER FUSULINIDEN-MEERE IM PERM. — Rep. sci. exp. N-W prov. China leadership Sven Hedin. — Sino-Swedish Exped. Public. **52**, — V. Invertebrate Paleontology **4**, — Stockholm, 1974, — 10 + 148 p., 2 photoplates, 1 table, 2 figures.

An old debt is payed off by the author in describing 15 Fusulinid species collected from 7 locations by NORIN, H. during the Sven Hedin-expedition in the year 1931. On the basis of this description the layers including the aforementioned Fusulinids were devided among the Lower and Upper Asselian, Sakmarian and/or Lower-Artinskian horizons of the Early-Permian. This description, made by the co-author of the "*Fossilium* Catalogus" of the Fusulinids, however modern, should be considered as a routine work only, if it was not amalgamated with the comparative analysis of the Fusulinid-based stratigraphical classification of all significant marine sequence in the Permian. The author points out, that the Fusulinid-bearing sequences have disappeared earlier in Japan as compared to South China, inspite of the fact, that the Permian and the Lower Triassic is separated by a hiatus in China too. The Late Permian is composed of beds consisting of evaporitic rocks in the USA, while in the Russian Platform and in the Ural Mountains the layers involved consist partly of evaporitic rocks partly of red beds of continental origin. Uninterrupted sedimentation between the Upper Permian and Lower Triassic is, however, a rather rare phenomenon even in the Paleotethys area and has not yet been proved by fossils suitable for long-distance correlation. Easy to access cases for the uninterrupted Carboniferous-Permian sedimentation are known mainly in Europe.

The author's most important statement is that there was not any close genetic connection between the Middle Permian, SE-Asian type-Fusulinid fauna of the marine sequences of the Paleotethys and those in Texas, because the latter existed in that time already as a paleographical unit, located separately from the Permian of the Paleotethys. Projecting the area characterized by the existence of Fusulinids upon the Pangea of DIETZ—HOLDEN, it can be seen that: *1)* excepting the sea-branches of the Ural-Mountains and Northern Canada, the seas in the Lower and Middle Permian were only the shelf-regions (*i.e.* marginal seas) of the Panthalassa; *2)* the connections of the SE Asian sea to the sea in Western America through Central Asia and Ural Mountains as well as Northern Canada still existing at the beginning of the Permian, ceased to exist later on. It means that the west coasts of the American continents emerged and some faunal elements from SE Asia could get into the epicontinental sea of the Midcontinent only occasionally and through the territory

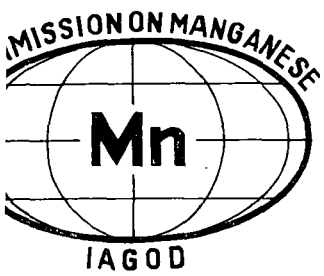
of the recent British Columbia only. The further regression and the spreading of the hypersaline facies finally resulted in the extinction of the Fusulinids.

As a consequence of the facts listed above *the division of the Permian in Eurasia should be independent of that of the "Midcontinent", and the three parts of the former should be defined on the basis of the appearance and duration of faunal waves of SE Asian character.* According to this the Lower Permian is characterized by assemblages of the Pseudofusulina-Pseudoschwagerina-Misellina-, and the Middle Permian by that of the Cancellina-Neoschwagerina-Lepidolinaline, *while the Upper Permian is marked by the presence of the Palaeofusulina and Codonofusiella genera, which are partly aberrant, but survived the Lower amd Middle Permian genera listed above.* The possibility of correlating the American division to the Eurasian one is created by the appearance of some SE Asian faunal elements in the sequences of the Midcontinent. As a consequence of this, the *Leonardian* together with the Wolfcampian in America would belong to the Lower Permian, the *Word, Capitan* and *Marble Canyon* formations would form the Middle Permian, while the overwhelming majority of the *Ochoan* formation would be pigeon-holed to the Upper Permian. According to the brand-new correlation of profiles in Western Serbia, in Velebit mountains and in the Carnian Alps carried out mainly by V. KOCHANSKY DEVIDÉ, KAHLER' s Lower Permian would comprise the lower part of the *Grödenian* stage (or that of the "Velebit beds" being correlated to the former) besides the *Rattendorfian* and *Trogkofelian* stages. The Middle Permian would contain the bulk of the *Grödenian* beds (or the Neoschwagerina-Yabeina-bearing part of the "Velebit sequence"); while the Upper Permian would be filled by the *Bellerophon-bearing* or *Žažarian* stage (as counterpart of the *Lopingian* in China).

In Hungary, this division is more favourable, as it strongerly accentuates a Late Permian deposition for the limestone and dolomite sequence in Nagyvisnyó (Bükk-Mts., NE-Hungary), as opposed to the Capitan even Word relations sometimes over-emphasized up to now. Thus the acception of KAHLER's ideas seems to be quite justified for the Hungarian geologists.

PROF DR. K. BALOGH

Acta Mineralogica-Petrographica, Szeged, XXII/1, 189—192, 1975



LETTERS OF THE COMMISSION ON MANGANESE (IAGOD)

INFORMATION ON THE IGCP PROJECT (74/II/111): GENESIS OF MANGANESE ORE DEPOSITS

GY. GRASSELLY and I. M. VARENTSOV
President Secretary

On behalf of the IAGOD Commission on Manganese the President of the Commission submitted a project proposal to the Board of the International Geological Correlation Programme (UNESCO-IUGS) entitled "Genesis of Manganese Ore Deposits". The main objective of this project would be a comparative study of manganese ore deposits of different origin including the study of their geological, mineralogical, geochemical and palaeogeographical peculiarities and their relations to prospecting methods as well as the summary of the modern methods of analysis applied to the manganese ores and minerals, respectively.

The IGCP Board at its third session in London, 21—24 April 1975, accepted the project under category A within the IGCP as defined at the second session of the Board (see Geological Correlation No. 2, 1974, p. 8), that is as a key project, in priority area 4 (Sources of energy and minerals).

The IGCP Board is looking forward to see the working group of this project in the framework of the IGCP being established on the occasion of the 25th International Geological Congress in Sydney in 1976.

Present state of the project

The project "Genesis of Manganese Ore Deposits" is in the initial stage of its development. It is mostly based on the activity and results of the Commission on Manganese of the International Association on the Genesis of Ore Deposits (IAGOD).

The Commission on Manganese has been established by the present president of the Commission in 1967 at the 2nd Symposium of the IAGOD, in St. Andrews, Scotland. Since that time the Commission organized technical sessions in 1970 in Tokyo during the IMA-IAGOD Meeting, in 1972 in Montreal on the occasion of the 24th International Geological Congress and in 1974 in Varna during the 4th Symposium of the IAGOD. Reports on the activity of the Commission on Manganese (IAGOD), and on its technical sessions and business meetings were yearly published in the "Letters of the Commission on Manganese (IAGOD)" in the volumes of the Acta Mineralogica-Petrographica, Szeged, Hungary, vol. XIX—XXI/2 (1969—1974), which is the semi-official organ of the Commission.

On the basis of the results obtained and the increasing international interest in the activity of the Commission, the Commission on Manganese decided to organize the 2nd International Symposium on the Geology and Geochemistry of Manganese during the 25th IGC, 1976, Sydney, Australia.

At the same time a successful programme was achieved in preparing an International Monograph on the Geology and Geochemistry of Manganese summarizing in three volumes the advances in the field of geology, mineralogy, geochemistry of manganese during the last twenty years, i.e. since the Mexican Symposium on Manganese (1956).

The Editorial Board of the Monograph and the Commission on Manganese, respectively, received till now 60 abstracts of papers to be presented at the technical sessions and published in the Monograph, respectively.

The 25th International Geological Congress offers the possibility to start this project, to outline the tasks of the future, to establish the co-operation on a broad international scale with countries, institutions and individuals interested in this field of research, to organize the working groups and to prepare a detailed working programme.

Scope of the project

The title "Genesis of Manganese Ore Deposits" denotes only in general the main direction of the project, in reality the project comprehends the different topics of the geology, mineralogy and geochemistry of manganese and the associated heavy metals taking into consideration that the processes of ore formation are not isolated from the geological and geochemical background in space and time. The project includes also the study of modern analytical methods applicable to the investigation of manganese ores and minerals, respectively, as well as the methods of prospection.

The Commission on Manganese intending to prepare a fruitful consultation of scientists concerned with the progress of the project mentioned during the 25th IGC, presents some basic objectives for deliberation and requests comments, recommendations of institutions, organizations or individuals having the intention to take part in this project.

The main subject areas denoted only on the whole may be:

a) Distribution and enrichment of manganese, processes of ore formation, their conditions and controlling factors
   i) Manganese in magmatic processes
   ii) Manganese in the hydrosphere
   iii) Manganese in the weathering zone
   iv) Manganese in sedimentary formations
   v) Manganese in metamorphic formations
   vi) Classification and characteristics of manganese ore deposits

b) Modern instrumental methods of analysis to the investigation of manganese ores and minerals, respectively,

c) Methods of prospection

Grouping the subject areas from another aspects is also possible, e.g.:

1. Manganese in Precambrian formations
2. Manganese in geosyncline formations
3. Manganese in platform formations
4. Manganese deposits on continental margin zones with special reference to global tectonics

5. Manganese in the main structural zones of the World Ocean with special reference to the results of deep sea drilling material
6. Manganese in the weathering zone with special reference to lateritization phenomena
7. Evolution of manganese deposits in the main structural zones of the Earth Crust

It should be noted the two versions above concerning the possible subject areas of the project are not yet completed and are considered merely as guidelines for discussion.

The Commission on Manganese requests the IGCP National Committees, organizations, institutions and individuals, respectively, having the intention of taking part in the project, to send their criticism, comments, recommendations and proposals concerning

a) the fundamental idea of the project
b) the subject areas mentioned
c) the subject areas with which the programme should be completed
d) the major unsolved problems in specific subject areas
e) subject panels to be organized to consider programme proposals in each of the subject areas

to the President of the Commission on Manganese up to April 1, 1976.

Activities foreseen for 1976

After having received the recommendations, proposals requested, the Commission on Manganese will be able to draft a more detailed, preliminary project programme including the main subject areas, the specific recommendations for study of different problems in each of the subject areas and panel groups concerned with specific subject areas.

This preliminary project programme will be sent before the 25th IGC to IGCP National Committees, institutions, individuals expressed their intention to take part in the project by forwarding their proposals and recommendations requested to the President of the Commission on Manganese.

This preliminary project programme will be discussed at the statutory meeting of the project at the 25th IGC, 1976, in Sydney, with the aim to formulate the strategy for the further development and co-ordination of the project.

The Commission on Manganese suggests that the deliberation of some basic questions, in connection with the discussion of the subject areas, would be desirable:

a) A review of present knowledge on the geology and geochemistry of manganese ore deposits of different genesis.
b) A critical selection of the major unsolved problems and the possibilities how and where these might be investigated.
c) Programme of investigation for the further research work including suggestions for major field activities and major laboratory research.
d) Consideration of possibilities of division of research work and co-operation, respectively, among the participating countries, institutions and individuals, resp.

As to the item a) it is hoped that the International Monograph on the Geology and Geochemistry of Manganese which is in preparation will give a fairly good summary on the present knowledge on the geology and geochemistry of manganese ore deposits. The Symposium on the Geology and Geochemistry of Manganese on the

occasion of the 25th IGC offers the possibility to review the most important results and to discuss thoroughly the items b—d supported by the preliminary programme drawn up by compiling the recommendations, proposals requested from the participants.

It is hoped that the previous activity and experiences of the IAGOD Commission on Manganese as well as the ever increasing co-operation of scientists of different countries in the activity and scientific meetings of the Commission will be a good starting basis for the further development of the new IGCP project: Genesis of Manganese Ore Deposits.

Any comments, proposals and recommendations are highly appreciated.

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TABLE 1

Chemical composition of the Lake Szappanosszék and that of the ground-waters from the bores in the neighbourhood

Sampling point	The water of the Szappanosszék		Lake Kondor, borehole No. 1		Lake Kondor, borehole No. 2		Lake Kondor, borehole No. 6		Lake Kondor, borehole No. 8		Lake Kondor, borehole No. 4		Lake Kondor, borehole No. 7		Lake Szappanosszék, borehole No. 12		Lake Szappanosszék, borehole No. 11		Lake Szívósszék, borehole No. 13		Lake Hattyússzék, borehole No. 17		Lake Hattyússzék, borehole No. 16	
Chemichal characteristics	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent pet cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent	mg/l	THAN's ionic equivalent per cent
Sodium Na^+	5 689.2	97.19	140.2	59.92	108.9	27.32	22.3	10.58	48.1	17.67	264.6	53.13	239.4	64.91	400.2	55.63	3421.3	97.56	252.7	47.76	1080.2	88.58	256.5	68.75
Potassium K^+	184.0	1.85	9.0	2.26	8.3	1.22	0.8	0.22	2.0	0.43	9.6	1.13	5.5	0.87	16.5	1.35	120.0	2.01	1.6	0.18	31.3	1.51	4.5	0.71
Calcium Ca^{++}	traces	—	53.1	26.03	160.7	46.26	98.9	53.79	95.0	40.6	54.0	12.44	49.2	15.30	6.4	1.02	traces	—	124.8	27.07	16.0	1.50	54.0	16.60
Magnesium Mg^{++}	29.6	0.96	14.6	11.79	53.1	25.19	39.5	35.40	60.2	41.83	87.7	33.29	36.9	18.91	159.8	41.99	7.8	0.42	69.9	24.98	54.2	8.40	27.5	13.93
Iron Fe^{++}	traces	—	traces	—	—	—	—	—	—	—	traces	—	—	—	—	—	—	—	—	—	—	—	traces	—
Ammonium NH^-	traces	—	—	—	—	—	—	—	traces	—	traces	—	traces	—	—	—	traces	—	—	—	traces	—	—	—
Chloride Cl^-	1 631.7	18.08	74.2	20.55	67.2	10.93	3.2	0.98	97.7	23.28	39.4	5.13	46.8	8.22	66.8	6.02	975.2	18.03	150.6	18.46	368.2	19.58	92.8	16.13
Hydrogen-carbonate HCO_3^-	3 282.7	21.13	427.1	68.73	499.1	47.17	528.4	94.34	463.7	64.19	1199.6	90.73	771.2	78.74	1300.9	68.11	2092.9	22.48	646.8	46.06	2262.5	69.89	818.8	82.66
Carbonate CO_3^{--}	4 059.6	53.15	—	—	—	—	—	—	—	—	—	—	—	—	166.8	17.76	2400.4	52.46	—	—	—	—	—	—
Sulphate SO_4^{--}	934.0	7.64	52.4	10.71	448.8	41.89	20.6	4.68	71.2	12.52	43.0	4.13	100.4	13.03	121.8	8.10	514.0	7.02	392.0	35.47	268.0	10.52	9.4	1.20
Meta-silica H_2SiO_3	3.1	—	17.9	—	19.7	—	22.9	—	19.7	—	18.7	—	14.8	—	8.0	—	—	—	17.9	—	22.9	—	14.5	—
Total dissolved solids	15 813.9	100.00	788.5	99.99	1265.8	99.99	736.6	100.00	857.6	99.99	1716.6	99.99	1264.2	99.99	2247.2	99.99	9531.6	99.99	1656.3	99.99	4103.3	99.99	1278.0	99.99
Alkalinity	189.10		7.00		8.18		8.66		7.60		19.66		12.46		26.88		114.30		10.60		37.08		13.42	
Total hardness in N°	6.80		10.78		34.71		22.92		27.14		27.73		15.37		37.65		1.79		33.54		14.70		13.88	
Carbonate hardness in N°	—		—		22.90		—		21.28		—		—		—		—		29.68		—		—	
Chemical reaction to phenolphtaleine	Alkaline		Acid		Acid		Acid		Acid		Acid		Acid		Alkaline		Alkaline		Acid		Acid		Acid	

CONTENTS

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